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MEASUREMENTS OF NO_2, HONO, NO_3, HCHO, PAH, NITROARENES AND PARTICULATE MUTAGENIC ACTIVITIES DURING THE CARBONACEOUS SPECIES METHODS COMPARISON STUDY

Final Report

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ABSTRACT

To allow for methods development and methods intercomparisons prior to the 1987 Southern California Air Quality Study, the California Air Resources Board funded two methods intercomparison studies, one in 1985 at Claremont concerning the measurement of nitrogenous species, and a second at Citrus College, Glendora, during August 1986 dealing principally with measurement methods for organic and carbonaceous species. In the Carbonaceous Species Methods Comparison Study (CSMCS) at Citrus College, Glendora, the Statewide Air Pollution Research Center conducted measurements of the ambient concentrations of several inorganic and organic species. Specifically, the following measurements were made:

- Using long pathlength differential optical absorption spectroscopy (DOAS), we measured nitrogen dioxide (NO_2), nitrous acid (HONO), and formaldehyde (HCHO).

- Using long pathlength Fourier infrared (FT-IR) absorption spectroscopy, we measured nitric acid (HNO_3), ammonia (NH_3) and HCHO.

- Ambient air samples were collected during 12-hr daytime and 12-hr nighttime periods onto Tenax solid adsorbent, polyurethane foam plugs and Teflon-impregnated glass fiber filters, and these samples were analyzed for mutagenicity and gas- and particle-associated polycyclic aromatic hydrocarbons (PAH) and nitroarenes.

An extensive data set for the gas-phase concentrations of NO_2, HONO, HNO_3, HCHO, NH_3 and the NO_3 radical was obtained (by DOAS and/or FT-IR spectroscopy), during this study period. Significant concentrations of these pollutants were observed, with ambient concentrations of up to approximately 140, 4.5, 30, 20 and 15 parts-per-billion (ppb) for NO_2, HONO, HNO_3, HCHO and NH_3, respectively. A definitive measurement of the time-concentration profile of NO_3 radicals was made on only one night during this study, with a peak NO_3 radical concentration of 70 parts-per-trillion (ppt) being measured on the night of August 13. The presence of NO_3 radicals, at levels <40 ppt, was observed on the evenings of August 13, 19 and 20.

Ambient particulate organic matter (POM) was collected on a 12-hr daytime and nighttime sampling period (0800-2000 and 2000-0800 PDT) and was tested for mutagenicity towards Salmonella typhimurium strains TA98 (with and without added S9), TA98NR (-S9) and TA98/1,8-DNP_6 (-S9). The mutagen densities obtained were consistent with those we have measured previously in the South Coast Air Basin. As also observed previously, the mutagen densities and mutagenic activity of the POM measured in the presence and absence of S9 were essentially indistinguishable, with average mutagen densities (rev m^{-3}) of 33 and 35 towards strain TA98, with and without S9, respectively, and a maximum of 61 rev m^{-3} (TA98, -S9).

Ambient air was also sampled on filters and solid adsorbents to collect the gas- and particle associated PAH and nitroarenes for combined gas chromatography-mass spectrometry analysis. The following PAH and nitroarenes were observed and quantified: naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benz(a)anthracene, chrysene/triphenylene, benzo(a)pyrene, 1- and 2-nitronaphthalene, 3-nitrobiphenyl, 2-, 3- and 8-nitrofluoranthene, and 1- and 2-nitropyrene.

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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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GLOSSARY OF TERMS, ABBREVIATIONS AND SYMBOLS

ARB	California Air Resources Board
atm	Atmosphere (pressure)
BaP	Benzo(a)pyrene
$BaP\text{-}d_{12}$	Deuterated benzo(a)pyrene
^{o}C	Degrees Centigrade
CH_2Cl_2	Dichloromethane
CH_3CN	Acetonitrile
CH_3OH	Methanol
cm	Centimeter
CSMCS	Carbonaceous Species Methods Comparison Study
DMSO	Dimethyl sulfoxide
DOAS	Differential optical absorption spectroscopy
EPA	U.S. Environmental Protection Agency
eV	Electron volt
^{o}F	Degrees Fahrenheit
$FL\text{-}d_{10}$	Deuterated fluoranthene
ft	Feet
FT-IR	Fourier-transform infrared absorption spectroscopy
g	Gram
GC	Gas chromatograph, gas chromatography, or gas chromatographic
GC-MS	Gas chromatography-mass spectrometry
GF filters	Glass fiber filters
HCHO	Formaldehyde
HCOOH	Formic acid
Hi-vol	High volume sampler

GLOSSARY OF TERMS
(continued)

HNO_3	Nitric acid
H_2O	Water
HONO	Nitrous acid
HPLC	High performance liquid chromatography
hr	Hour
Hz	Hertz (cycle s^{-1})
I	Light intensity
I_o	Initial light intensity
i.d.	Internal diameter
K	Thousand
K	Degrees Kelvin
km	Kilometer
L-broth or LB-broth	Growth medium for overnight culture of *Salmonella* strains
m	Meter
m^3	Cubic meter
M	Molar
MeOH	Methanol
mg	Milligram
$MgCl_2$	Magnesium chloride
MID	Multiple ion detection technique, used together with GC-MS
min	Minute
min^{-1}	Per minute
mL	Milliliter
mm	Millimeter

GLOSSARY OF TERMS
(continued)

mol	mole (6.022×10^{23} molecules)
MS	Mass spectrometer
m/z	Mass to charge ratio
Mutagen density	Atmospheric mutagenicity "concentration"; total activity divided by sampling volume (rev m^{-3})
Mutagen loading	Specific mutagenicity of the particulate matter; total activity divided by particulate weight (rev mg^{-1})
m.w.	Molecular weight
NBS SRM 1648	National Bureau of Standards, Standard Reference Material 1648, urban dust collected in St. Louis, MO
NBS SRM 1649	National Bureau of Standards, Standard Reference Material 1649, urban dust collected in Washington, D.C.
NF	Nitrofluoranthene
ng	Nanogram (10^{-9} gram)
NH_3	Ammonia
NH_4NO_3	Ammonium nitrate
Nitroarenes	Nitrated polycyclic aromatic hydrocarbons (PAH)
nm	Nanometer (10^{-9} meter)
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_3	Gaseous nitrate radical
NO_x	Oxides of nitrogen ($NO + NO_2$)
N_2O_5	Dinitrogen pentoxide
NP	Nitropyrene
O.D.	Optical density
OH	Hydroxyl radical
O_3	Ozone

GLOSSARY OF TERMS
(continued)

Open column chromatography	Liquid chromatography technique, used for compound separation or purification
PAH	Polycyclic aromatic hydrocarbons
PDT	Pacific daylight time
PER-d_{12}	Deuterated perylene
pg	Picogram (10^{-12} gram)
pH	$-\log_{10}[H^+]$; $[H^+]$ = hydrogen ion concentration in mol ℓ^{-1}
PER	Perylene
POM	Particulate organic matter
ppb	Part per billion
ppt	Part per trillion
PUF	Polyurethane foam
PY-d_{10}	Deuterated pyrene
rev	Revertants; net response above background in the Salmonella mutagenicity test
S9	Supernatant from a 9000 x g centrifugation of rat liver homogenate
SAPRC	Statewide Air Pollution Research Center
SCE	Southern California Edison
SCFM	Standard cubic feet per minute
Semi-prep column	Semi-preparative scale column used for compound separation or purification by HPLC
Specific activity	Specific mutagenicity of the particulate extract; slope of the Salmonella dose-response curve (rev μg^{-1})
TA98	Ames Salmonella typhimurium strain, detects frameshift mutations. Most sensitive strain for detecting ambient particulate mutagens
TA98NR	Nitroreductase-deficient isolate of strain TA98; less sensitive than TA98 to many mononitroarenes

GLOSSARY OF TERMS
(continued)

TA98/1,8-DNP$_6$	Transacetylase-deficient isolate of strain TA98; less sensitive than TA98 to dinitropyrenes
Tenax-GC	Solid adsorbent used for the collection of volatile organics
TIGF filters	Teflon impregnated glass fiber filters
Total activity	The product of specific activity and total extract weight for a given collection period (rev)
UCR	University of California, Riverside
µg	Microgram (10^{-6} gram)
µℓ	Microliter (10^{-6} liter)
µm	Micrometer (10^{-6} meter)
µmol	Micromole (10^{-6} mole)
uv/vis	Ultraviolet/visible
W	Watt

I. PROJECT SUMMARY

The chemical processes leading to the production of ozone from the reactive organic gases and oxides of nitrogen precursors are complex, and it is necessary to have measurements of the reactant and product species in as detailed a manner as possible in order to provide a data base suitable for input into airshed computer models. These organic compounds may be distributed between the gas and particle phases, and hence measurements of their concentrations in both phases must be carried out. In order to allow for a methods development and methods intercomparison prior to the 1987 Southern California Air Quality Study (SCAQS), the California Air Resources Board (ARB) funded two methods intercomparison studies, one in 1985 at Claremont concerning the measurement of nitrogenous species, and a second at Citrus College, Glendora, during August of 1986 dealing principally with the intercomparison of measurement methods for organic and carbonaceous species.

In the Carbonaceous Species Methods Comparison Study (CSMCS) at Citrus College, Glendora, the Statewide Air Pollution Research Center (SAPRC) carried out the measurement of several inorganic and organic species. Specifically, the following measurements were made:

- Using long pathlength differential optical absorption spectroscopy (DOAS), we measured nitrogen dioxide (NO_2), nitrous acid (HONO), and formaldehyde (HCHO).
- Using long pathlength Fourier infrared (FT-IR) absorption spectroscopy, we measured nitric acid (HNO_3), ammonia (NH_3) and HCHO.
- Ambient air samples were collected during 12-hr daytime and 12-hr nighttime periods onto Tenax solid adsorbent, polyurethane foam (PUF) plugs and Teflon-impregnated glass fiber (TIGF) filters, and these samples analyzed for mutagenicity and gas- and particle-associated polycyclic aromatic hydrocarbons (PAH) and nitroarenes.

The DOAS and FT-IR systems utilized 25 m base-path multiple-reflection optical systems aligned parallel to one another, with the optical beams being ~2.4 m above the ground surface. An extensive data set for the gas-phase concentrations of NO_2, HONO, HNO_3, HCHO (by both DOAS and FT-IR spectroscopy), NH_3 and the NO_3 radical was obtained during this study period. The complete data set is tabulated in detail in Sections IV

and V of this report, and Figures I-1 and I-2 show the HCHO, HNO_3 and NH_3 time-concentration profiles obtained by FT-IR spectroscopy (Figure I-1) and the HONO time-concentration profile as monitored by DOAS (Figure I-2), respectively. These two figures and the data presented in Sections IV and V show that significant concentrations of these pollutants were present during this sampling period, with ambient concentrations of up to approximately 140, 4.5, 30, 20 and 15 ppb for NO_2, HONO, HNO_3, HCHO and NH_3, respectively. A definitive measurement of the presence of NO_3 radicals was made only on one night during this study (due to the detection limit for this species), with a peak NO_3 radical concentration of 70 ppt being measured on the night of August 13. The presence of NO_3 radicals, at levels <40 ppt, was observed on the evenings of August 13, 19 and 20.

Ambient particulate organic matter (POM) was collected on a 12-hr daytime and nighttime sampling period (0800-2000 and 2000-0800 PDT) and was tested for mutagenicity towards Salmonella typhimurium strains TA98 (with and without added S9), TA98NR (-S9) and TA98/1,8-DNP_6 (-S9). The measured mutagen densities, in revertants per m^3 of air sampled, are given in Table I-1. These mutagen densities are consistent with those we have measured previously in the South Coast Air Basin. As also observed previously, the mutagen densities and mutagenic activity of the POM measured in the presence and absence of S9 are essentially indistinguishable, with average mutagen densities (strain TA98) of 33 and 35 rev m^{-3}, with and without S9, respectively.

Ambient air was also sampled on filters and solid adsorbents in order to collect the gas- and particle associated PAH and PAH-derivatives for combined gas chromatography-mass spectrometry analysis. Three collection systems were used to sample ambient air: low and high-flow (1 and 10 L min^{-1}, respectively) cartridges packed with Tenax-GC solid adsorbent to sample the volatile PAH such as naphthalene and the methylnaphthalenes; Teflon-impregnated glass fiber (TIGF) filters backed up by polyurethane foam (PUF) plugs to sample the semi-volatile PAH and nitroarenes present either in the gas phase or blown-off the filters during the collection period; and TIGF filters for the collection of POM containing the higher molecular weight, low-volatility, PAH and nitroarenes. The following PAH

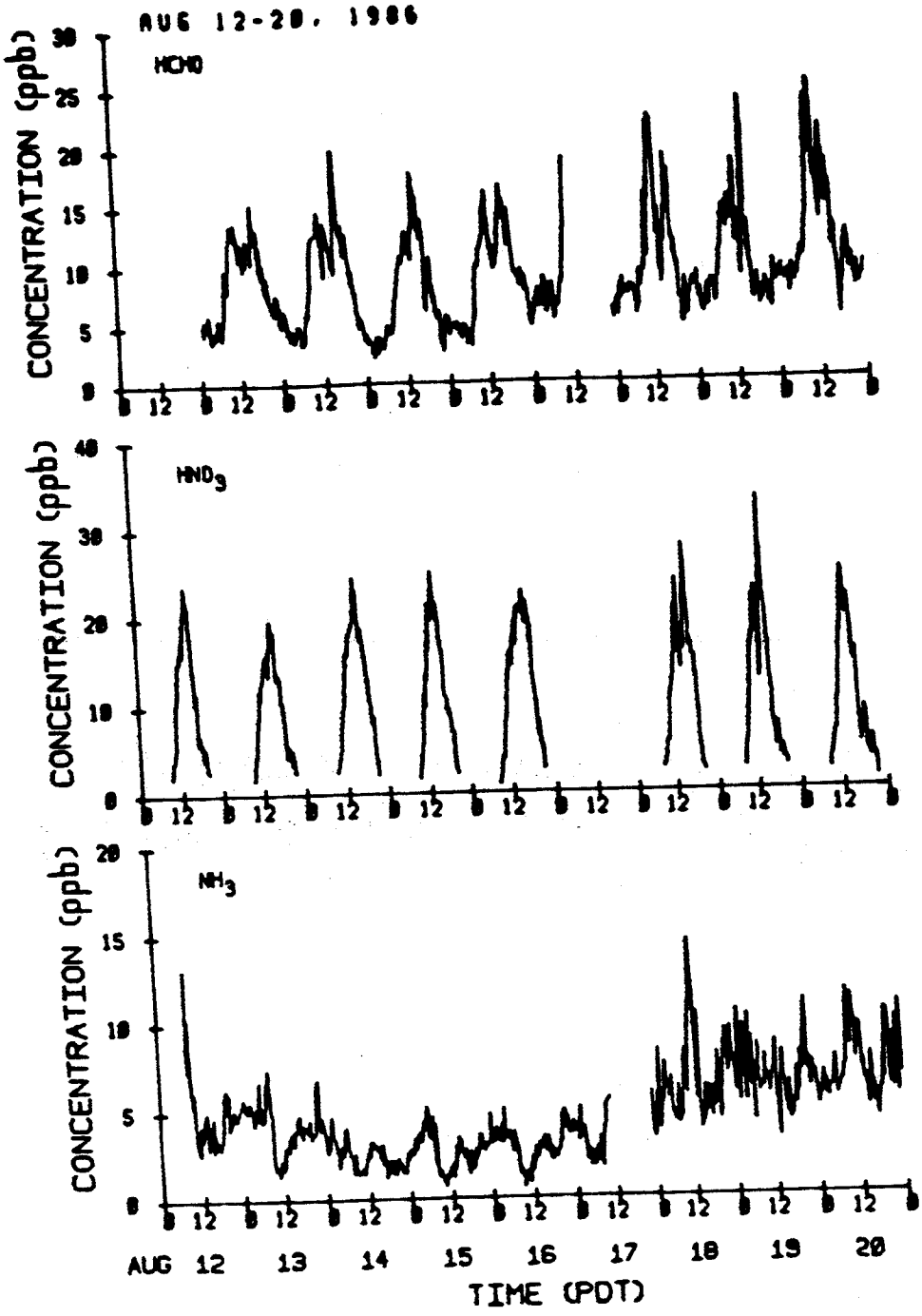


Figure I-1. Time-concentration profiles for formaldehyde, nitric acid and ammonia measured by long pathlength FT-IR spectroscopy during the 1986 Citrus College study.

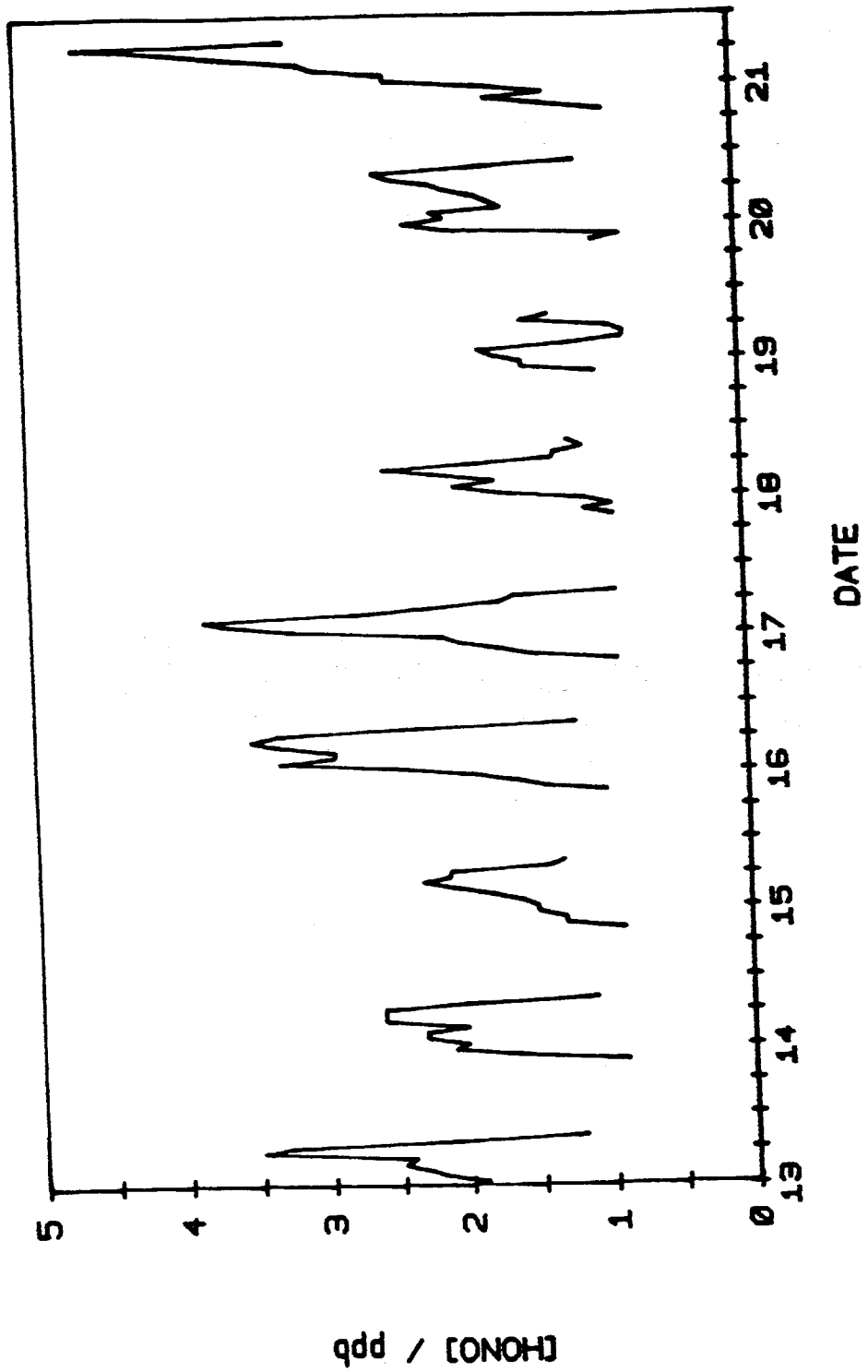


Figure I-2. Nitrous acid time-concentration profiles measured by long pathlength DOAS system at Citrus College (Glendora) in August 1986.

Table I-1. Particulate Mutagen Densities, Citrus College, August 1986

Date	Time of Day (PDT)	Mutagen Density (rev m^{-3}) TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
8/12/86	0800-2000	42[a]	39[a]	17[a]	9.2[a]
8/12-13/86	2000-0800	31	30	15	6.5
8/13/86	0800-2000	27	22	7.8	3.3
8/13-14/86	2000-0800	44	44	25	10
8/14/86	0800-2000	33	35	15	6.8
8/14-15/86	2000-0800	15	11	6.5	3.5
8/15/86	0800-2000	28	27	11	5.1
8/15-16/86	2000-0800	31	41	21	10
8/16/86	0800-2000	28	29	12	4.9
8/16-17/86	2000-0800	40	40	19	8.3
8/17/86	0800-2000	27	27	11	4.5
8/17-18/86	2000-0800	40	43	22	9.5
8/18/86	0800-2000	42	53	23	7.6
8/18-19/86	2000-0800	15	13	7.4	2.9
8/19/86	0800-2000	33	35	12	5.3
8/19-20/86	2000-0800	38	43	18	8.5
8/20/86	0800-2000	55	61	21	10
8/20-21/86	2000-0800	28	28	13	5.4

[a]Sampling volume ~5% low due to power failure.

and nitroarenes were observed and quantified: naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benz(a)-anthracene, chrysene/triphenylene, benzo(a)pyrene, 1- and 2-nitronaphthalene, 3-nitrobiphenyl, 2-, 3- and 8-nitrofluoranthene, and 1- and 2-nitropyrene. The ambient concentrations of these PAH and nitroarenes are presented in Section VI and, as an example Figures I-3 and I-4 show the time-concentration profiles of naphthalene and 1- and 2-methylnaphthalene, respectively, during this study period.

This study site was also chosen by the ARB staff to be one of the seven locations in California at which sampling was to be conducted to obtain data concerning the ambient levels of mutagenicity and of PAH (including PAH derivatives such as the nitro-PAH) to which populations were exposed. The Glendora site was chosen as the site impacted by vehicle emissions. The mutagenicity data and the concentrations of the PAH and PAH-derivatives observed at this site are hence an integral part of our ongoing study "A Survey of Ambient Concentrations of Selected Polycyclic Aromatic Hydrocarbons (PAH) at Various Locations in California" (ARB Contract No. A5-185-32), and a full discussion of the data and the conclusions to be drawn from the entire data set collected at the seven sites throughout California will be presented in the final report to that program.

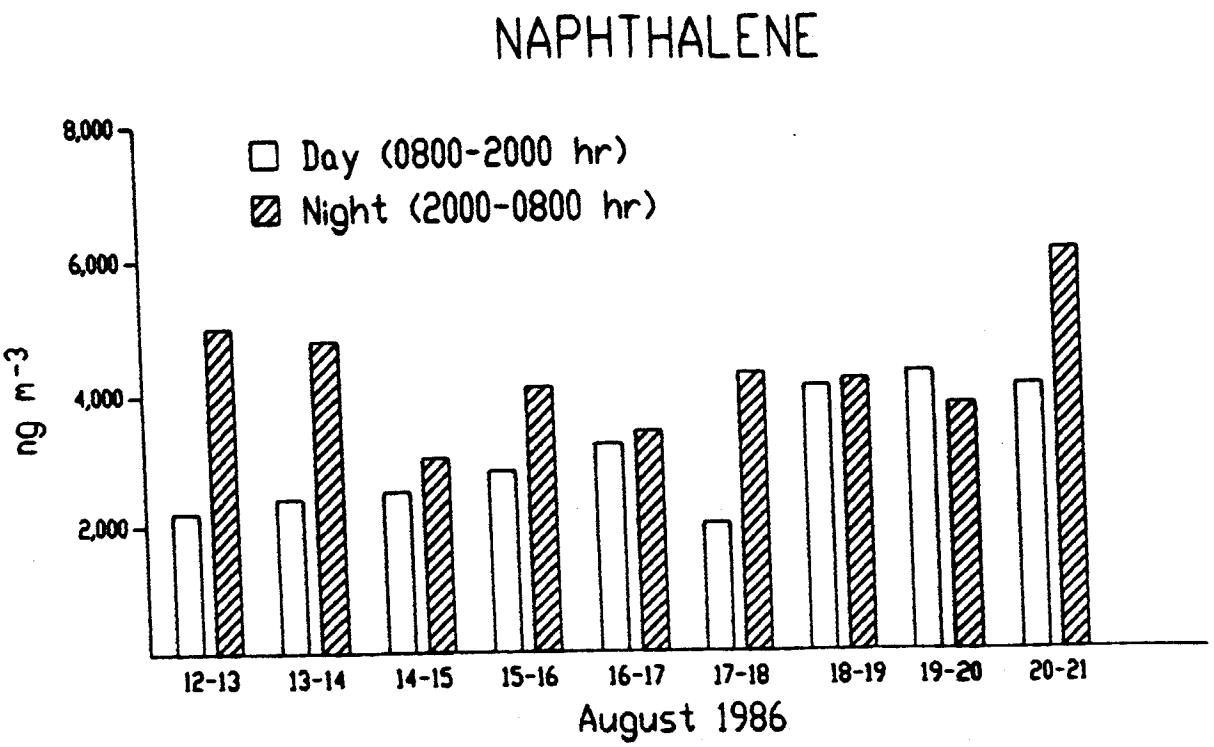


Figure I-3. Diurnal variations in naphthalene concentration at Citrus College in Glendora, CA.

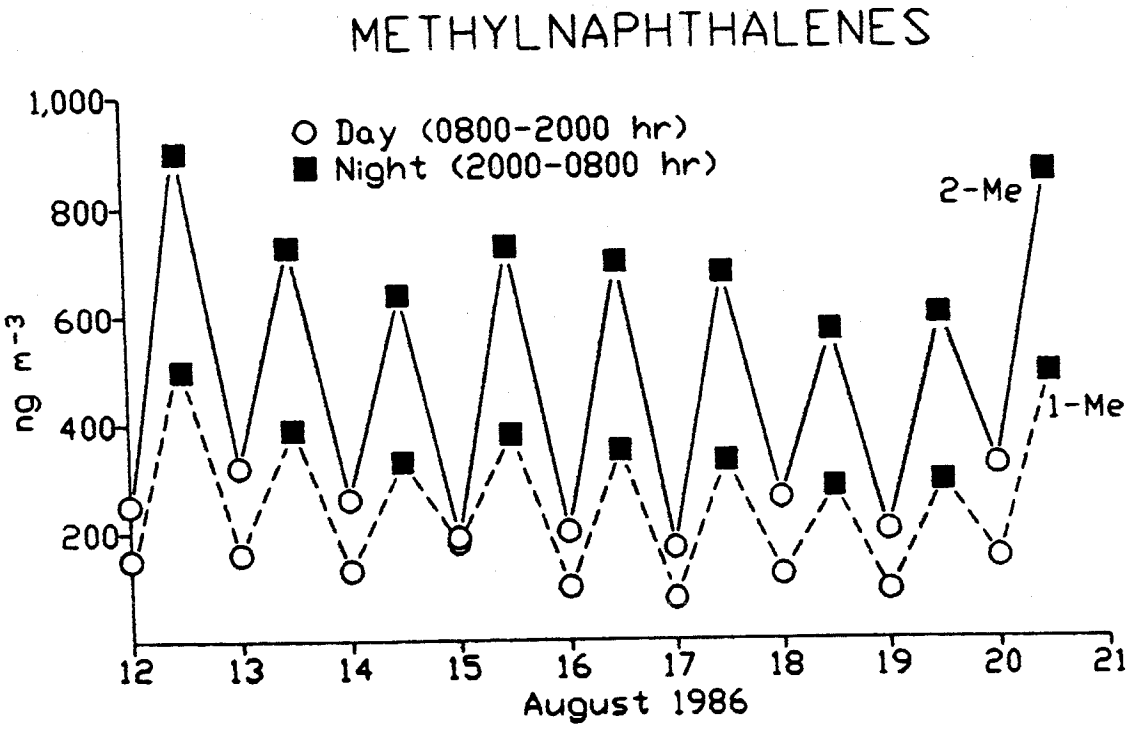


Figure I-4. Diurnal variation in the concentrations of 1-methylnaphthalene (1-Me) and 2-methylnaphthalene (2-Me) at Citrus College in Glendora, CA.

II. INTRODUCTION

The chemical processes leading to the production of ozone from the reactive organic gases and oxides of nitrogen precursors are exceedingly complex, and in order to provide a data base suitable for input into airshed computer models it is necessary to have measurements of the reactant and product species in as detailed a manner as possible. Since these organic compounds may be distributed between the gas and particle phases, measurements of both the gas- and particle-phase concentrations of organic chemicals must be carried out. In order to allow for a methods development and methods intercomparison prior to the 1987 Southern California Air Quality Study (SCAQS), the California Air Resources Board (ARB) funded two methods intercomparison studies, one in 1985 at Claremont concerning the measurement of nitrogenous species, and a second at Citrus College, Glendora, during August of 1986 dealing principally with the intercomparison of measurement methods for organic and carbonaceous species.

In this Carbonaceous Species Methods Comparison Study at Citrus College, Glendora, the Statewide Air Pollution Research Center (SAPRC) was involved in the measurement of a number of inorganic and organic species. Specifically, we measured the atmospheric concentrations of the following compounds:

- Using long pathlength differential optical absorption spectroscopy (DOAS), we measured nitrogen dioxide (NO_2), nitrous acid (HONO), and formaldehyde (HCHO).
- Using long pathlength Fourier infrared (FT-IR) absorption spectroscopy, we measured nitric acid (HNO_3), ammonia (NH_3) and HCHO.
- Ambient air samples were collected during 12-hr daytime and 12-hr nighttime periods onto Tenax solid adsorbent, polyurethane foam (PUF) plugs and Teflon-impregnated glass fiber (TIGF) filters, and these samples analyzed for mutagenicity and gas- and particle-associated polycyclic aromatic hydrocarbons (PAH) and nitroarenes.

Furthermore, the measurements of the ambient atmospheric concentrations of PAH and PAH-derivatives at Citrus College formed one part of a further ambient measurement study funded by the ARB (Contract No. A5-185-32) dealing with the ambient concentrations of PAH and PAH-derivatives at

seven sites throughout California impacted by differing combustion emission sources. The Citrus College site served as the vehicle emission-impacted site for this study.

The description of the site at Citrus College, Glendora, and the experimental procedures and data obtained from these measurement methods are detailed in the following sections.

III. DESCRIPTION OF SITE

As noted earlier, this monitoring program was conducted in conjunction with the ARB-funded Carbonaceous Species Methods Comparison Study. As shown in Figure III-1, the ARB selected a site adjacent to the football stadium on the campus of Citrus College for this study. The orientation and relationship of the long pathlength FT-IR and DOAS systems to other investigators is shown in Figure III-2. The SAPRC high-volume (Hi-vol) samplers were located just north of the mobile vans and trailers of other investigators. The optical spectrometers were elevated on concrete blocks to achieve a 2.4 m (8 ft) height for the optical beams, in order to minimize the influences of dry deposition of nitric acid and other nitrogenous species. This requirement necessitated a major restructuring of the FT-IR and DOAS instrument supports. In order to augment the 1.2 m (4 ft) height initially designed into the optical axes of both of the long pathlength mirror assemblies, while at the same time preventing extraneous vibrations, the spectrometers, mirror systems and their housings were set on massive concrete blocks.

Six 4 ft x 4 ft x 10 ft concrete structures were rented from the Pyramid Precast company, which provided the necessary machinery to position the blocks on premarked areas at the study site. Three of these blocks constituted the support platform for the FT-IR and DOAS assemblies at each end of the optical path (see Figure III-2). New 9 ft x 12 ft sheds were procured and constructed on these platforms during the last week of August and the first week of September. Subsequent assembly and testing of the spectrometers and optical systems was completed in time for the scheduled start of the field study on September 11, 1985.

As shown in Figure III-2, the two SAPRC 25 m basepath optical systems were set up parallel to each other and to the scaffolding which supported most of the samplers from other groups participating in the intercomparison study. The optical systems were aligned in a north-south orientation to minimize scattered light problems at sunrise and sunset, and positioned due west of the scaffolding and various mobile vans and trailers.

The study period began at 0800 PDT on Tuesday, August 12 and continued until 0800 PDT on August 21. The FT-IR and DOAS systems operated essentially continuously during this period, with FT-IR spectra being

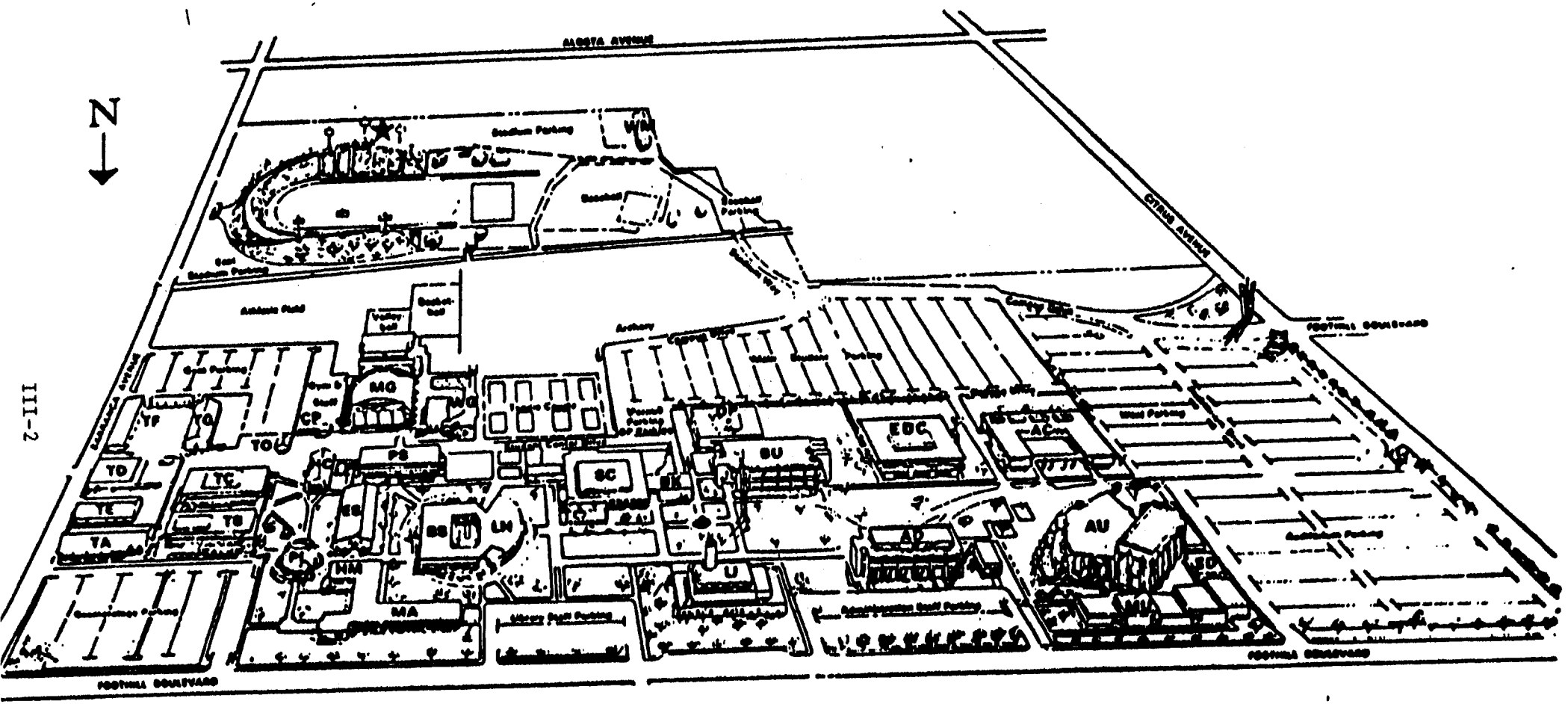


Figure III-1. Citrus College campus showing location of August 1986 field study adjacent to football stadium. ★ - Field study site.

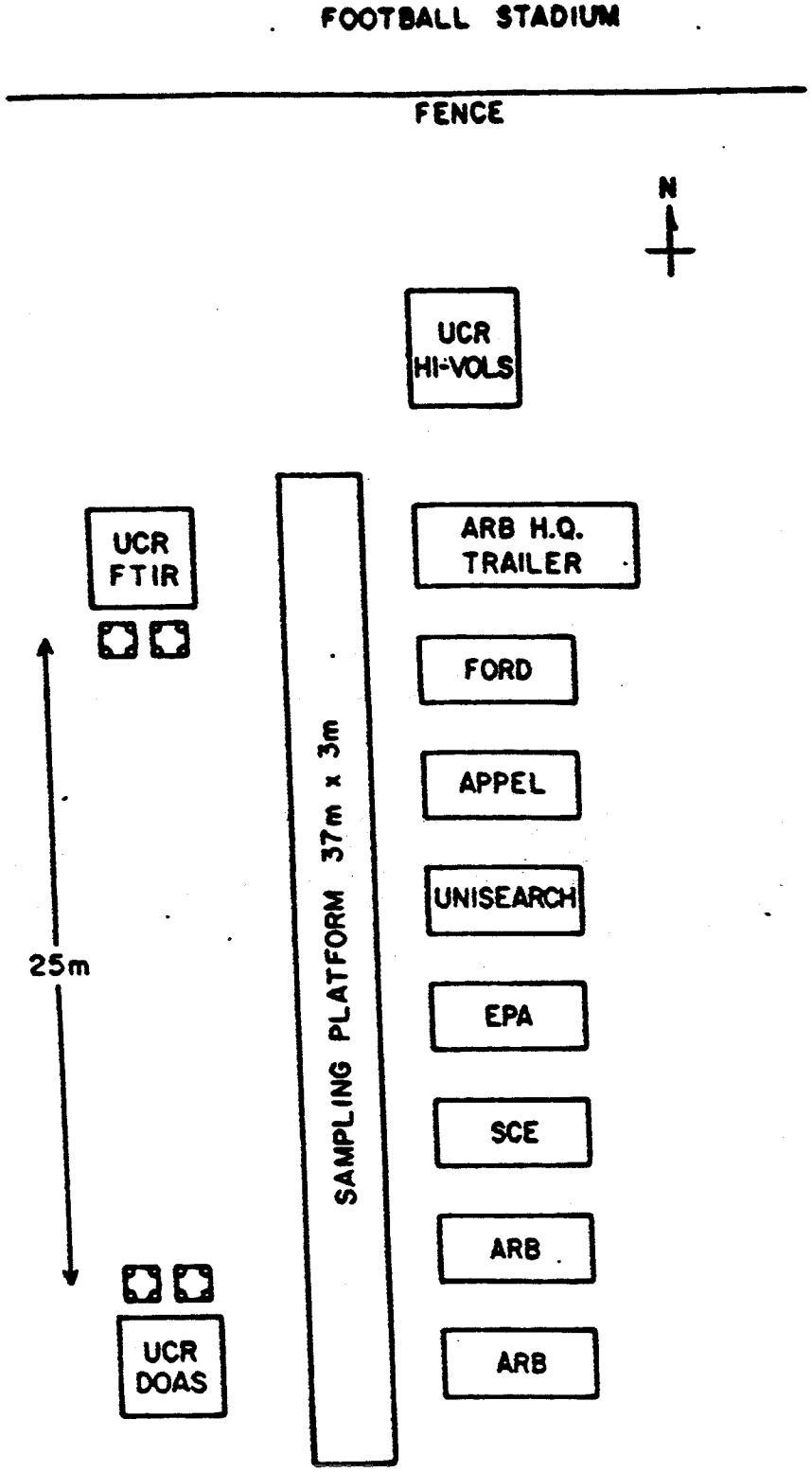


Figure III-2. Positions of the longpath FT-IR and DOAS systems and UCR Hi-vols relative to the instruments of the other participants in the Carbonaceous Aerosol Study on the Citrus College campus, August 1986.

acquired every 12-15 minutes during the day and every 20 minutes at night; DOAS spectra were acquired approximately every 15 minutes day and night. The Hi-vol samplers and other associated experiments operated on the 12-hr time periods 0800-2000 PDT and 2000-0800 PDT.

IV. MEASUREMENTS OF HONO, NO_2, NO_3 RADICALS AND HCHO BY DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY

A. Introduction

The development of a long pathlength DOAS system by Perner and Platt (1979) and its application and extension by these workers and by SAPRC researchers (Platt et al. 1980a,b, 1981, 1982, 1984, Harris et al. 1982, Pitts et al. 1984a,b, 1985a) has provided a technique capable of sensitive, specific, and time-resolved measurements of the ambient concentrations of a number of important atmospheric species, including nitrous acid, formaldehyde, the nitrate radical and nitrogen dioxide.

In this section, we briefly describe the design and operation of the 25 m basepath DOAS system employed to measure ambient levels of NO_3 radicals, HONO, NO_2 and HCHO during the Carbonaceous Species Methods Comparison Study and the results obtained during this measurement period. A more detailed description of the experimental system is provided in an earlier report to the ARB (Winer et al. 1987).

B. Experimental Methods

The 25 m basepath optical system (Figure IV-1) was of the three-mirror White design, but with an added corner reflector at the in-focus end which effectively doubled its maximum pathlength capability. The mirrors were fabricated from 30 cm dia. x 5 cm thick Pyrex blanks and coated with a custom dielectric coating for optimum reflectivity in the spectral regions of interest.

The DOAS system measures the ambient concentrations of trace components which have distinct vibronic structures by their light absorption in the near-ultraviolet (uv) and visible spectral regions. White light from a 75 W high pressure Xenon lamp was imaged by a spherical mirror into the plane of the nesting (in-focus) mirror of the White cell and then propagated through the multiple reflection optics until it emerged from the system and was imaged onto the entrance slit of the monochromator (SPEX 1870 0.5 m). The light intensity was monitored by a photomultiplier (EMI 9659Q) and the signal acquired and averaged by a DEC MINC 11/23 minicomputer.

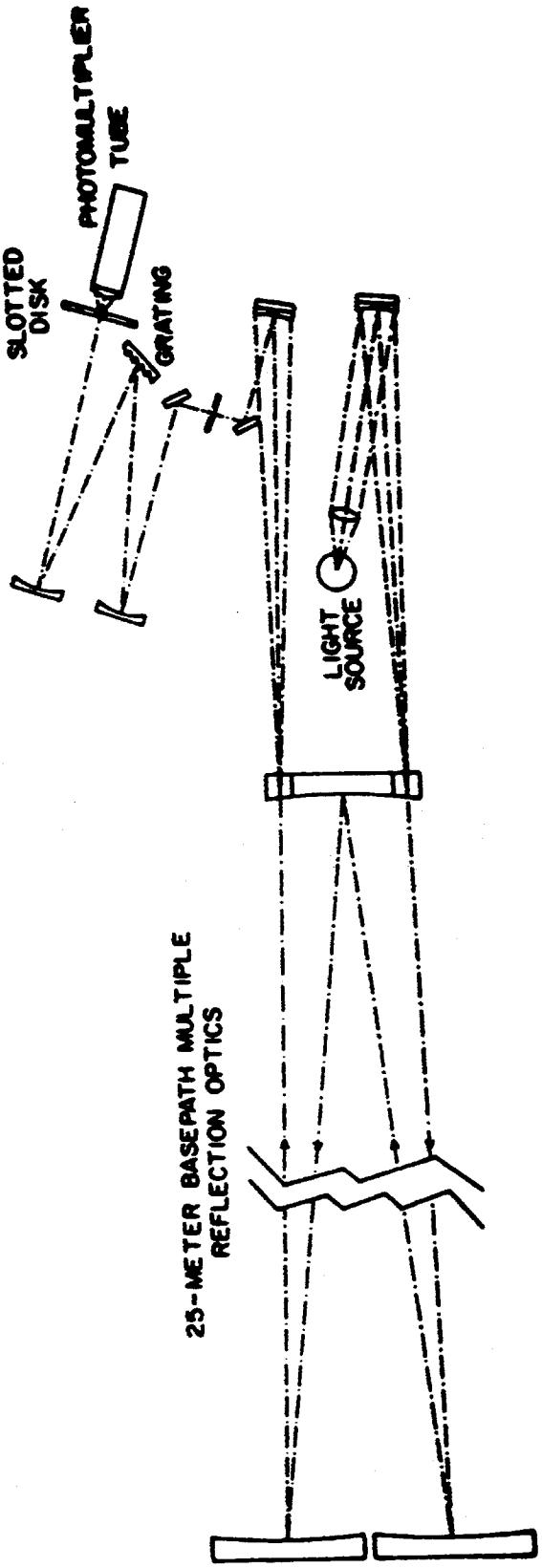


Figure IV-1. Schematic diagram of the longpath DOAS system.

With the DOAS, a rotating slotted disk was used to allow rapid scanning. The slotted disk was formed by etching a set of exit slits (100 μm wide, 10 mm spacing) radially into a thin metal disk. This disk was rotated in the focal plane of the dispersed spectrum. As each slit moved across the opening between the masks that block the two adjacent slits, it scanned a spectral range of ~30-60 nm, depending on the rotation frequency of the slotted disk. The orientation of the spectrometer grating determined which specific spectral region was scanned. As employed in its final form in this program the slotted disk rotated at ~4 Hz, resulting in a scan rate of ~100 Hz, well above the frequency distribution of atmospheric turbulence (which otherwise would introduce unwanted structure into the spectra).

As a slit became visible at the edge of the mask, it was detected by an infrared photodiode. A trigger signal was sent to the computer which continuously recorded digitized samples of the light intensity as the slit scanned across the spectrum. Since several tens of thousand such scans were acquired and added in the computer memory within a few minutes, this improved the signal-to-noise ratio of the resulting spectrum. The rotational speed of the slotted disk was maintained constant to within ±0.1% to preserve the spectral resolution while superimposing the scans. The computer was also used for spectral deconvolution and for the calculation of optical densities.

Since a single scan required only ~10 msec, atmospheric scintillation effects had little effect on the signal. Moreover, since typically (2-8) x 10^4 individual scans were recorded and signal-averaged over each several minute measurement period, even complete, but momentary, interruption of the light beam had no appreciable effect on the final spectrum. Except under the haziest conditions, stray light effects were negligible due to the instrument's narrow field of view [~8 x 10^{-5} steradians] and in any case stray light could be taken into account by means of appropriate background spectra.

The concentrations of atmospheric species were derived from Beer's Law. However, since the light intensity in the absence of any absorption (I_o) cannot be obtained with this technique, the differential optical density was employed and thus only those compounds which have structured absorption spectra could be measured. Table IV-1 gives the characteristic

absorption bands and detection limits for a number of atmospheric species of interest, based on a 1 km pathlength. It can be seen that the detection limits range from 3 ppb for HCHO down to ~10 ppt for the NO_3 radical. For automatic scanning of spectra, 32 or 40 reflections (corresponding to pathlengths of 800 and 1000 m, respectively) were generally employed, and the corresponding detection limits for quantitative analyses were then 0.6-0.7 ppb for HONO and 13-16 ppt for NO_3 radicals.

Table IV-1. Calculated Detection Limits for 25-m Basepath Multiple-Reflection Cell DOAS System Operated at 1 km Pathlength

Compound	Differential Absorption Coefficient (atm^{-1} cm^{-1})	Absorption Wavelength (nm)	Detection Limit (ppb) for 1 km and 2.5×10^{-4} O.D. (base 10)
NO_2	2.7	365	2.3
HONO	11	354	0.6
NO_3 Radical	480	662	0.01
SO_2	15	300	0.4
HCHO	2.1	339	3.0

C. Results and Discussion

The SAPRC 25 m basepath DOAS system was set up at the Glendora site in the specific orientation, relative to other experiments conducted during this field study, as described in Section III.

Essentially continuous DOAS measurements were conducted from August 13 until the morning of August 21, 1986. Maximum ozone levels and peak concentrations of NO_3 radicals during this study are summarized in Table IV-2. Individual concentrations of HONO, HCHO and NO_2 observed during this period are given in tabular form in Appendix B, and hourly average data for these species are given in Tables IV-3 to IV-5. For the majority of the time the pathlength was set to 800 m with a detection

Table IV-2. Maximum O_3 Levels and Observations of NO_3 Radicals at Citrus College, Glendora, CA, During August 13-20, 1986

Date	Maximum O_3 Concentration (ppm)	NO_3 Radical Peak Concentration (ppt)
8/13	0.185	72
8/14	0.27	<40
8/15	0.26	ND[a]
8/16	0.24	ND
8/17	0.27	ND
8/18	0.28	ND
8/19	0.30	<40
8/20	0.27	<40

[a]ND = Not detected.

limit equivalent to an optical density of 3×10^{-4}. The data reduction process was more automated than previously, and thus the detection limit was raised from 2×10^{-4} to 3×10^{-4} O.D. to offset the tendency of the software to interpret noise at the detection limit as a peak. The corresponding detection limits were: NO_2, 3.5 ppb; HONO, 0.8 ppb; and HCHO, 4.5 ppb.

Because the HONO and HCHO bands are overlapped by NO_2 bands and NO_2 is more abundant in the Los Angeles basin, the DOAS spectra must be first analyzed for NO_2 to enable its features to be quantitatively removed prior to determining HONO and HCHO concentrations. Figure IV-2 shows the time-concentration profile for NO_2 from 0000 PDT on August 13 to 0800 PDT on August 21. The solid line shows the DOAS data, while the dashed line shows measurements made by our chemiluminescence oxides of nitrogen analyzer. The two curves track each other very well during the nighttime and early morning hours. In the afternoon the NO_x analyzer consistently read 10 to 30 ppb higher; since the DOAS values at those times were as low as 15-25 ppb this caused a discrepancy of a factor of two or more. The higher values measured by the chemiluminescence method are attributed to

Table IV-3. Hourly Average HONO Concentrations (ppb)[a] Measured by the Long Pathlength DOAS System During the 1986 Citrus College Study

Time Period (hr) PDT	Date								
	8/13	8/14	8/15	8/16	8/17	8/18	8/19	8/20	8/21
00-01	1.9	2.0	1.5	2.4	3.2	1.7	1.7	2.0	2.4
01-02	2.2	2.3	1.6	3.3	3.6	2.0	1.8	2.1	2.4
02-03	2.3	2.3	1.8	2.9	3.8	1.7	1.2	1.6	2.9
03-04	2.5	2.0	2.0	2.9	2.7	2.1	BD[b]	1.7	3.0
04-05	2.4	2.6	2.3	3.3	2.3	2.5	BD	1.8	3.5
05-06	3.5	2.6	2.1	3.5	1.7	1.9	0.9	2.0	3.9
06-07	3.3	2.6	2.1	3.3	1.6	1.3	1.5	2.1	4.6
07-08	2.2	2.0	1.4	2.4	0.9	1.3	1.3	2.4	3.1
08-09	1.2	1.1	1.3	1.2	BD	1.1	BD	2.5	
09-10	BD	BD	BD	BD	BD	1.2	BD	1.8	
10-11	BD	BD	BD	BD	BD	BD	BD	1.1	
11-12	BD	BD	BD	BD	BD	BD	BD	BD	
12-13	BD	BD	BD	BD	BD	BD	BD	BD	
13-14	BD	BD	BD	BD	BD	BD	BD	BD	
14-15	BD	BD	BD	BD	BD	BD	BD	BD	
15-16	BD	BD	BD	BD	BD	BD	BD	BD	
16-17	BD	BD	BD	BD	BD	BD	BD	BD	
17-18	BD	BD	BD	BD	BD	BD	BD	BD	
18-19	BD	BD	BD	BD	BD	BD	BD	BD	
19-20	BD	BD	BD	0.9	BD	BD	BD	0.9	
20-21	BD	0.9	1.0	1.5	0.9	BD	1.0	1.3	
21-22	0.9	1.3	1.4	1.7	1.1	1.0	BD	1.7	
22-23	1.6	1.3	1.6	2.0	0.9	1.5	2.0	1.3	
23-24	2.1	1.5	1.9	2.1	1.1	1.5	2.3	1.7	

[a]Estimated errors: ±0.8 ppb or ±30%, whichever is larger.
[b]BD = Below detection limit (0.8 ppb).

Table IV-4. Hourly Average NO_2 Concentrations (ppb)[a] Measured by the Long Pathlength DOAS System During the 1986 Citrus College Study

Time Period (hr) PDT	Date								
	8/13	8/14	8/15	8/16	8/17	8/18	8/19	8/20	8/21
00-01	64.1	66.9	54.5	56.3	64.4	72.1	56.2	54.3	69.4
01-02	61.5	61.6	51.8	50.9	63.3	74.4	45.9	43.4	55.5
02-03	57.3	60.9	48.9	52.0	56.3	75.1	27.7	22.8	60.6
03-04	54.2	64.0	42.7	50.3	36.2	69.5	21.8	20.4	63.9
04-05	52.1	61.7	39.2	46.7	27.3	65.9	18.2	21.4	62.1
05-06	46.9	61.6	41.4	46.1	23.4	44.1	18.9	33.8	61.0
06-07	47.5	63.3	42.9	43.1	22.1	51.3	40.2	45.2	60.9
07-08	64.4	63.8	55.4	49.4	21.1	58.1	61.6	63.6	72.4
08-09	77.7	74.4	61.9	70.0	26.4	53.0	47.6	140.1	
09-10	93.6	76.8	65.0	68.3	48.3	82.8	49.5	118.5	
10-11	81.1	66.5	60.9	60.7	44.9	91.9	41.2	130.3	
11-12	57.1	50.8	53.0	47.1	33.3	90.6	32.5	50.7	
12-13	43.3	38.5	38.5	27.8	23.1	54.4	20.4	44.5	
13-14	42.2	33.2	31.1	14.4	16.8	20.2	26.3	25.7	
14-15	35.9	24.4	26.0	13.1	12.8	17.8	27.8	16.9	
15-16	36.8	28.4	43.8	14.2	17.7	25.0	29.8	29.9	
16-17	38.8	39.6	46.2	19.5	21.9	35.2	28.3	29.4	
17-18	42.4	41.1	51.6	33.2	26.0	47.7	42.7	37.6	
18-19	53.6	47.7	57.3	45.5	49.6	52.4	60.1	61.8	
19-20	62.1	59.6	70.3	62.6	74.3	52.1	85.2	88.7	
20-21	71.2	76.5	67.1	77.5	78.7	72.9	85.4	89.8	
21-22	75.3	77.4	60.6	81.3	70.3	77.3	77.7	85.5	
22-23	74.1	73.5	60.1	70.4	67.2	69.1	71.9	77.6	
23-24	70.8	61.1	60.5	66.9	70.6	65.7	66.0	83.7	

[a]Estimated errors: ±3.5 ppb or ±15%, whichever is larger.

Table IV-5. Hourly Average HCHO Concentrations (ppb)[a] Measured by the Long Pathlength DOAS System During the 1986 Citrus College Study

Time Period (hr) PDT	Date								
	8/13	8/14	8/15	8/16	8/17	8/18	8/19	8/20	8/21
00-01	7.3	5.8	5.6	5.7	10.3	5.7	7.6	9.2	11.0
01-02	6.9	5.8	6.0	7.3	8.9	6.9	8.1	10.0	8.8
02-03	6.4	5.2	6.0	5.4	8.8	7.8	8.1	9.4	9.9
03-04	6.2	5.5	5.5	6.4	8.9	8.6	7.0	10.5	10.1
04-05	5.8	5.5	5.5	6.3	7.1	7.4	8.1	10.2	9.6
05-06	6.3	5.4	6.1	6.7	7.3	7.5	8.5	10.7	10.8
06-07	6.4	6.7	6.2	6.1	7.2	7.3	10.5	9.1	11.6
07-08	9.7	7.4	8.3	7.3	8.8	8.9	11.2	13.1	13.9
08-09	11.0	11.2	8.9	8.7	9.7	9.6	11.3	19.9	
09-10	12.4	13.0	10.2	11.2	14.4	13.1	12.8	18.4	
10-11	12.7	14.0	11.7	11.1	15.4	14.3	12.3	16.1	
11-12	11.6	13.5	13.0	12.6	16.3	17.8	12.9	13.1	
12-13	12.2	12.8	12.7	10.7	14.8	13.8	12.1	16.8	
13-14	12.4	11.3	12.9	10.0	13.1	10.2	14.8	15.1	
14-15	13.8	10.0	16.1	11.2	12.2	7.9	14.6	14.4	
15-16	15.3	14.7	12.1	11.4	13.9	13.7	10.1	11.7	
16-17	14.9	13.5	10.9	12.0	12.0	13.2	7.0	9.2	
17-18	14.3	12.7	9.5	10.8	7.9	11.4	6.6	7.7	
18-19	10.2	11.1	8.3	7.9	7.1	7.8	5.9	9.3	
19-20	9.5	10.0	7.4	7.9	8.4	5.3	5.6	8.4	
20-21	9.1	8.5	5.7	8.3	7.5	5.8	6.4	7.6	
21-22	7.4	7.3	5.1	8.3	6.3	7.7	5.5	7.4	
22-23	8.1	6.3	5.1	6.5	7.2	7.2	9.2	7.0	
23-24	7.0	5.9	5.4	6.1	7.1	8.4	9.7	9.5	

[a]Estimated errors: ±4.5 ppb or ±30%, whichever is larger.

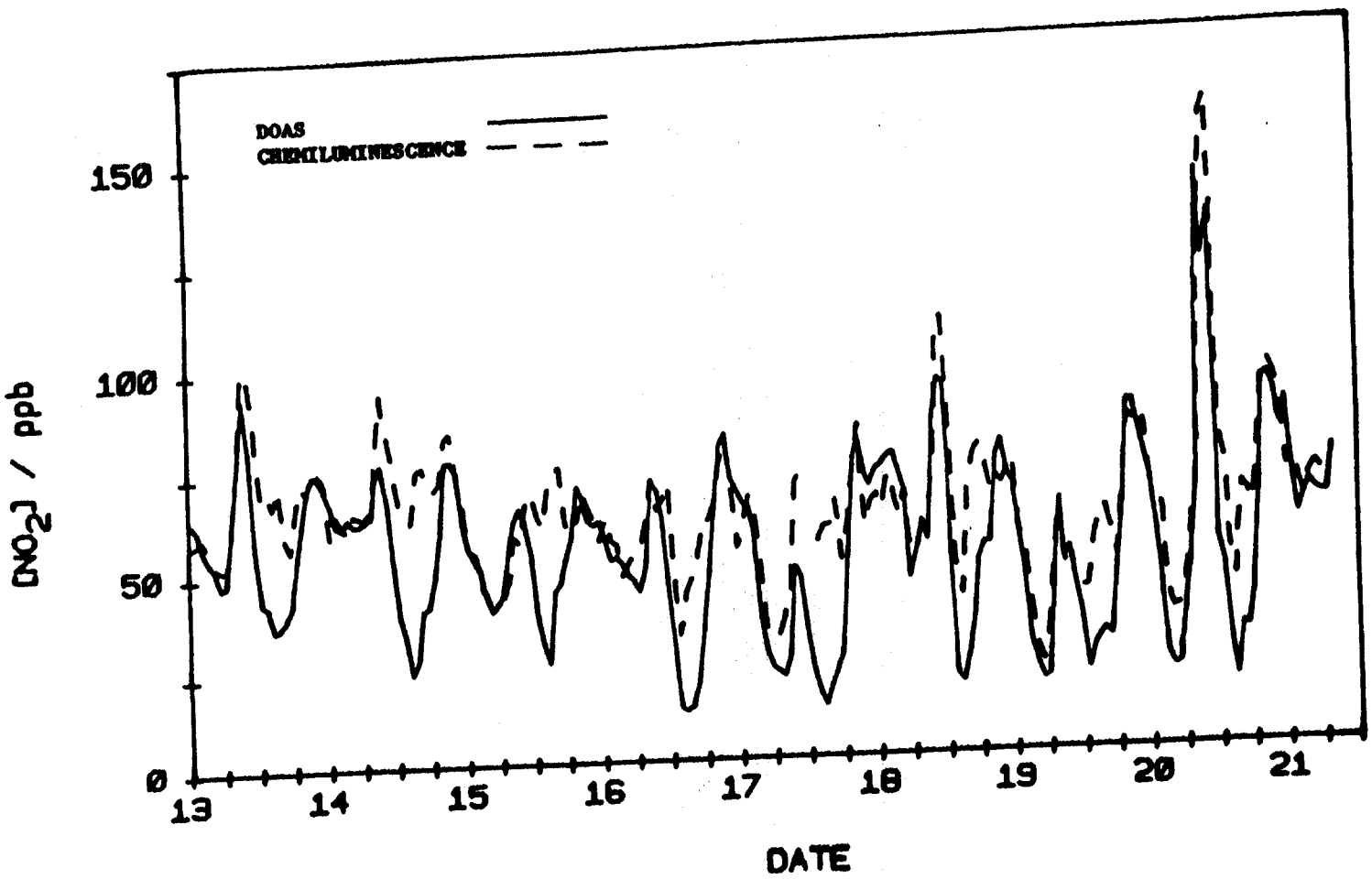


Figure IV-2. Time concentration profiles for nitrogen dioxide measured by DOAS and chemiluminescence (NO_x-NO) at Citrus College (Glendora) in August 1986.

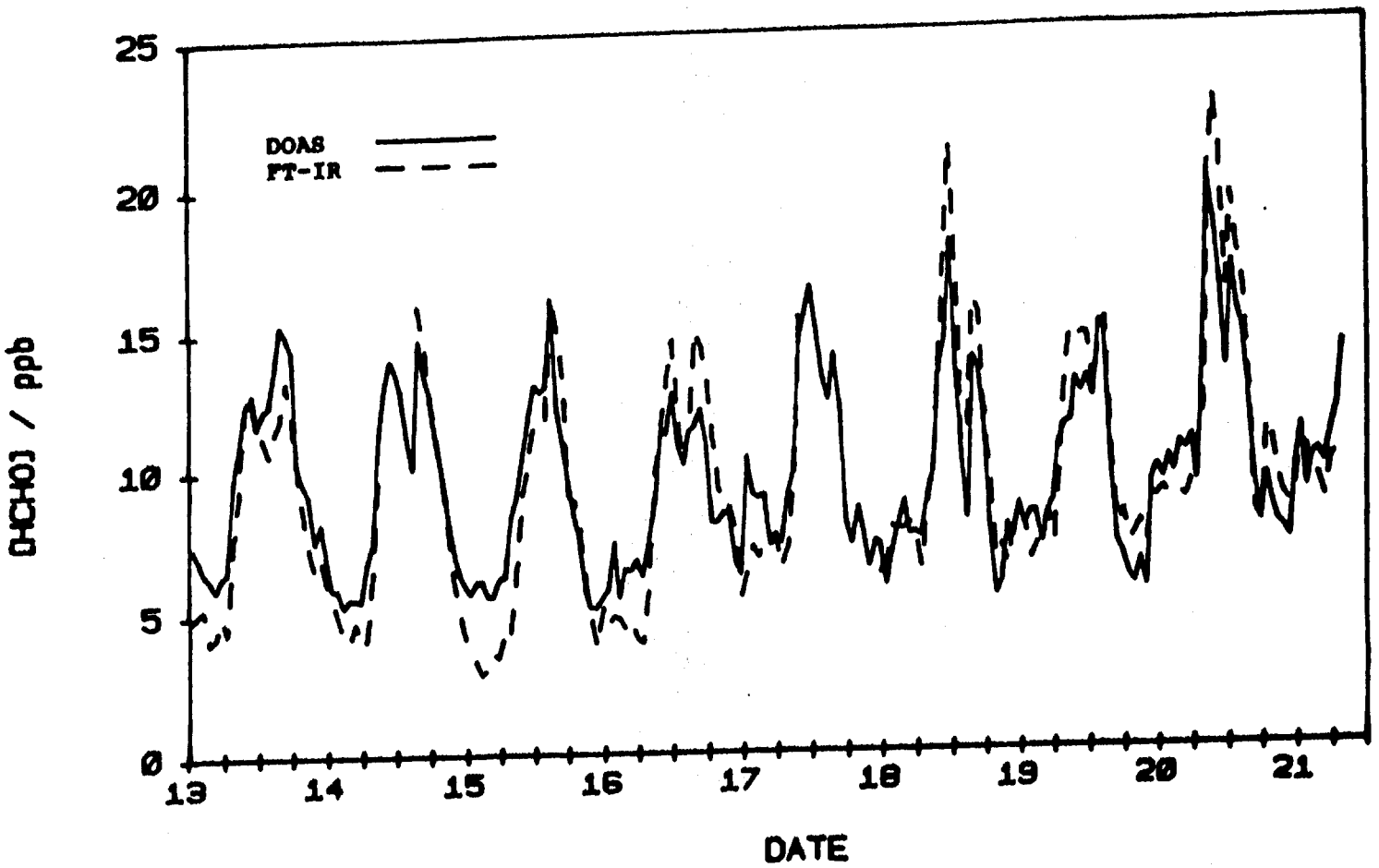


Figure IV-3. Time concentration profiles for formaldehyde measured by long pathlength DOAS and FT-IR spectrometers at Citrus College (Glendora) in August 1986.

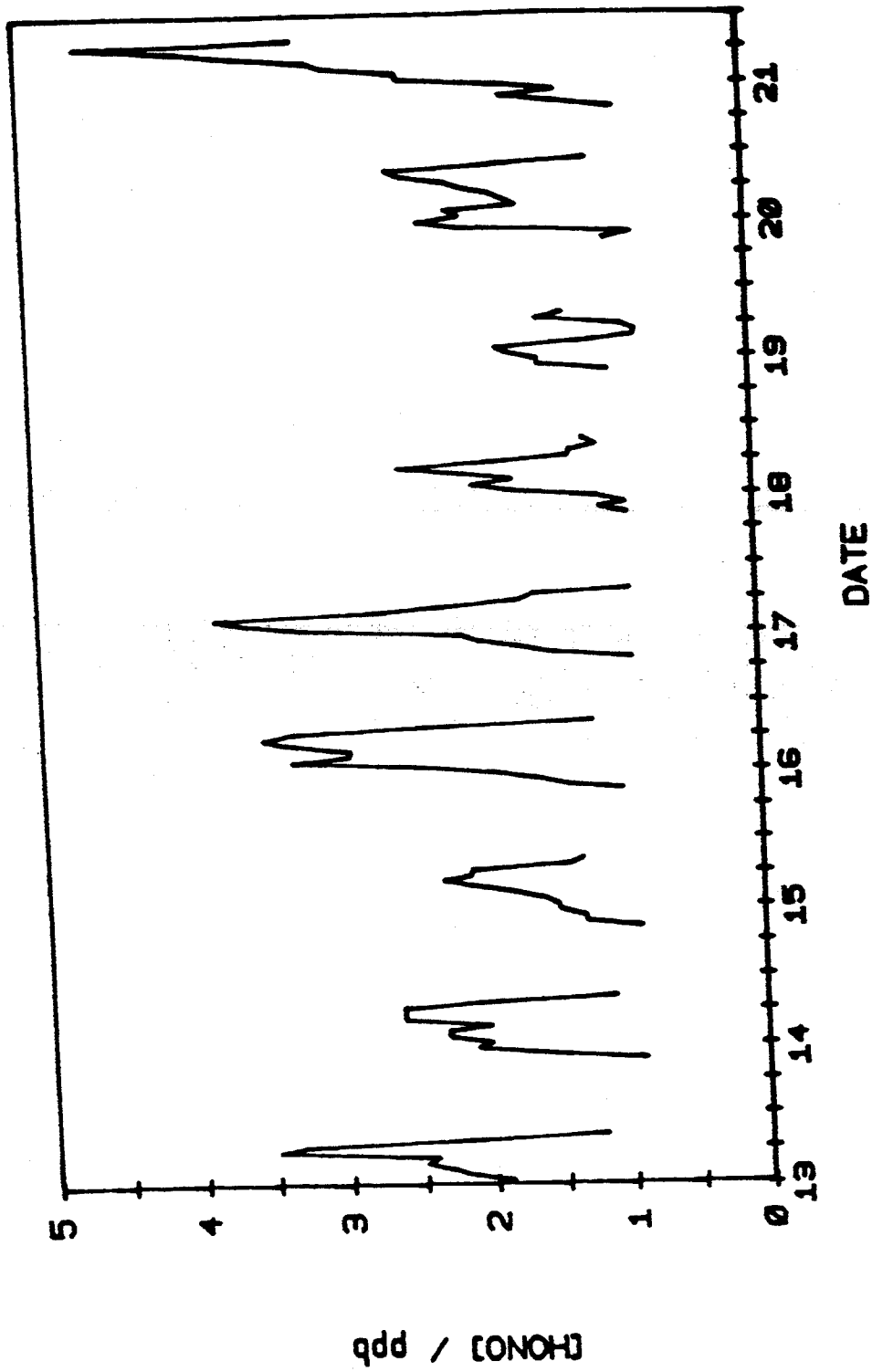


Figure IV-4. Nitrous acid time-concentration profiles measured by long pathlength DOAS system at Citrus College (Glendora) in August 1986.

the known interferences of HNO_3 and PAN in this detection method, consistent with the levels of HNO_3 and PAN in the afternoon periods being approximately equivalent to this difference in the DOAS NO_2 and chemiluminescence NO_x-NO readings.

After the quantitative removal of the NO_2 features from the DOAS spectra, the data reduction procedure utilized a simultaneous least-squares fit of HONO and HCHO reference spectra to the residual ambient air spectra. Figure IV-3 shows the time concentration profile for HCHO as determined by DOAS (solid line). For comparison, the FT-IR data from Section V are shown as the dashed line. The agreement between the two methods is very good, with the discrepancies being within the error limits. However, it appears that the DOAS results for the first four nights are consistently higher than the FT-IR data by about 1-3 ppb. This could be due to an overestimation of HCHO absorption features in the DOAS spectra, since the reported FT-IR HCHO levels were at or below the DOAS detection limit of 4.5 ppb (where the signal-to-noise ratio was near unity).

Finally, the HONO time-concentration profile for August 13-21 is presented in Figure IV-4. No comparison data are available for HONO for this study. However, as discussed above, the only source of a large systematic error would be the literature value for the HONO absorption cross-sections used in the calculations. During the Citrus College field study, nighttime HONO levels were higher than observed in the 1985 Nitrogen Species Methods Comparison Study at Claremont, where the maximum HONO concentrations were in the range 1.5 to 2.5 ppb. For five of the nights at Citrus College, the HONO concentrations were also in the same range. However, for three nights HONO levels attained ~3.5 ppb, and during the last night of the study HONO reached a maximum of 4.5 ppb. There was, however, no correlation of the HONO concentrations to the nighttime NO_2 levels, which were relatively constant at 60-75 ppb. Since the heterogeneous formation of HONO from NO_2 involves moisture, correlations to other parameters such as relative humidity and particulate loading may prove interesting.

V. LONG PATHLENGTH FT-IR MEASUREMENTS OF HNO_3, NH_3 AND HCHO

A. Introduction

As discussed elsewhere in more detail (Winer et al. 1987), the long pathlength FT-IR system was employed to provide benchmark data for the Nitrogen Species Methods Comparison Study held at Pomona College (Claremont) in September 1985. Following this, the FT-IR spectrometer participated in our winter field study at El Camino Community College (Torrance). Due to a need for a more detailed comparison of HNO_3 measurements by the FT-IR and tunable diode laser spectroscopic (TDLS) methods than had been possible during the 1985 Claremont study, the longpath FT-IR system was subsequently set up in Glendora on the Citrus College campus for more intensive measurements of HNO_3 and NH_3 between August 12-21, 1986. In this study, species coverage by the FT-IR method was extended to include the measurement of formaldehyde (HCHO). Attempts were also made to detect N_2O_5 in ambient air by thorough examination of the spectra recorded in the late afternoon and evening hours. Ammonia (NH_3) was included among the species measured since, in certain localities, it can profoundly affect the concentration of gaseous HNO_3 by its reaction to form aerosol ammonium nitrate (Doyle et al. 1979, Tuazon et al. 1980).

B. Experimental

1. Kilometer Pathlength FT-IR System

Measurements of ambient air pollutants by infrared spectroscopy were carried out using a recently constructed 25-m basepath, open multiple-reflection optical system interfaced to a Mattson Instruments, Inc., Sirius 100 FT-IR spectrometer. This spectrometer has a maximum resolution capability of 0.125 cm^{-1} and is equipped with a Motorola 68000-based data system. The long pathlength optics are of the three-mirror White design (White 1942), with provisions for adding a corner reflector at the in-focus end (Horn and Pimentel 1971), when desired, to effectively double the system's pathlength. The mirrors in this new optical system were fabricated from 30 cm diameter, 6 cm thick Pyrex blanks and gold-coated for the best reflectivity ($\geq$99%) in the infrared. The optimum pathlength for monitoring was determined to be in the 1-1.5 km range

during routine operation, although short-term use of optical paths greater than 2 km were possible.

As discussed in Section III, the long pathlength FT-IR spectrometer was operated alongside the long pathlength DOAS system, as shown in Figure V-1. The optical layout of the FT-IR system is presented in more detail in Figure V-2. The sets of mirrors of the two spectrometers were arrayed in opposite directions but aligned side by side in a compact arrangement which made possible simultaneous analyses of virtually the same air mass. The FT-IR spectrometer was housed in an air conditioned shed while the multiple reflection mirror assembly outside was shaded from direct sunlight by protective shields. While the spectrometer system had an initial height of 1.2 m (above ground level) designed into the optical axis this was raised to a total of 2.4 m (8 ft), the common sampling height required for all analytical techniques being compared during this field study. Massive concrete blocks were employed as support structures to attain this sampling height.

2. Acquisition of Spectra

Spectra were recorded at a pathlength of 1150 meters and 0.125 cm^{-1} resolution (unapodized). Sixty-four scans (interferograms) were added during a 4.5-min period and then transformed (calculation time of ~2.5 min) to a single beam spectrum. Each spectrum of 128 K points was truncated and the spectral region from 400 to 3000 cm^{-1}, which contained the absorption bands of HNO_3, NH_3 and HCHO used for analysis, was retained and archived.

Four to five spectra per hour were collected. This rate of data collection permitted a real-time examination of the quality of spectra being recorded and such checks were consistently made during daytime and early evening hours (0800-2200 PDT). During the "noncritical" period of 2200-0600 hours when nitric acid was expected to be below the detection limit, the FT-IR spectrometer was programmed to conduct automatic monitoring.

3. Calibration

Figure V-3 illustrates the absorption features of HNO_3 and NH_3 in the region accessible to long pathlength FT-IR measurements. Asterisks mark the peaks which were employed to determine concentrations. A more

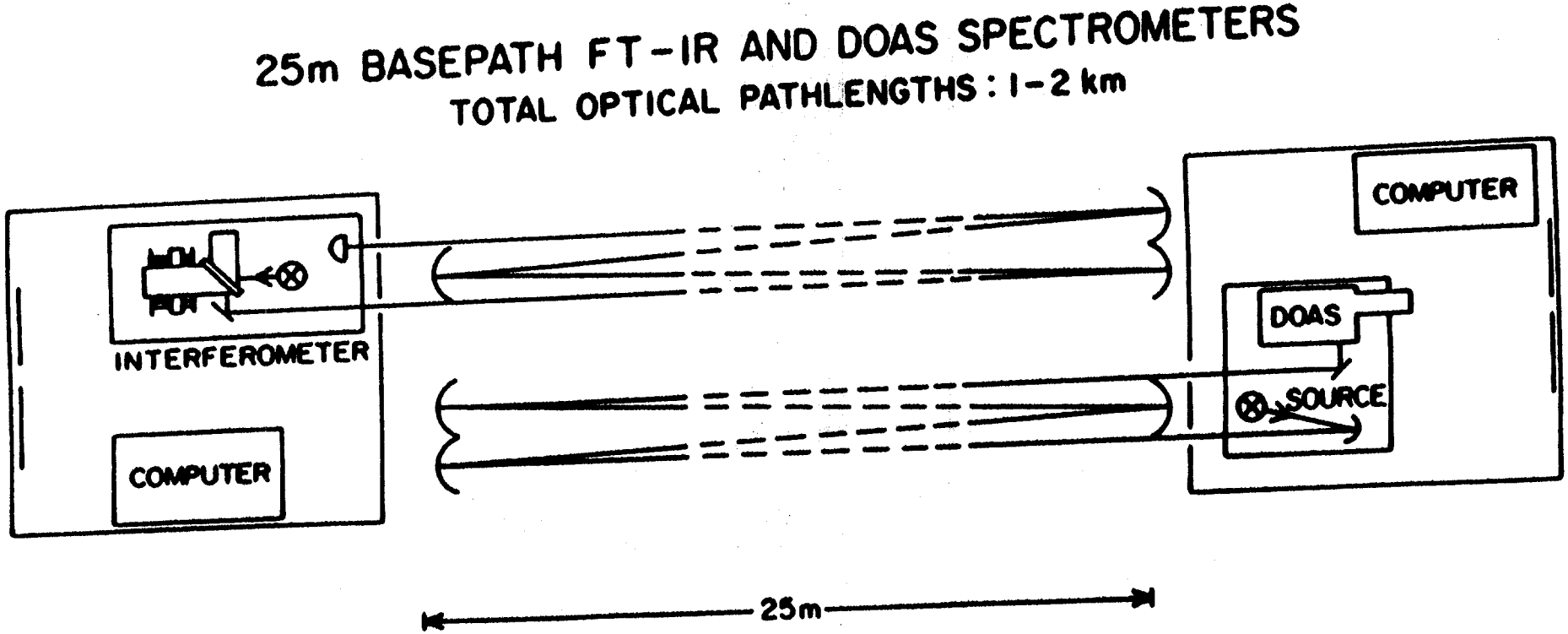


Figure V-1. Relative arrangement of the longpath FT-IR and DOAS systems.

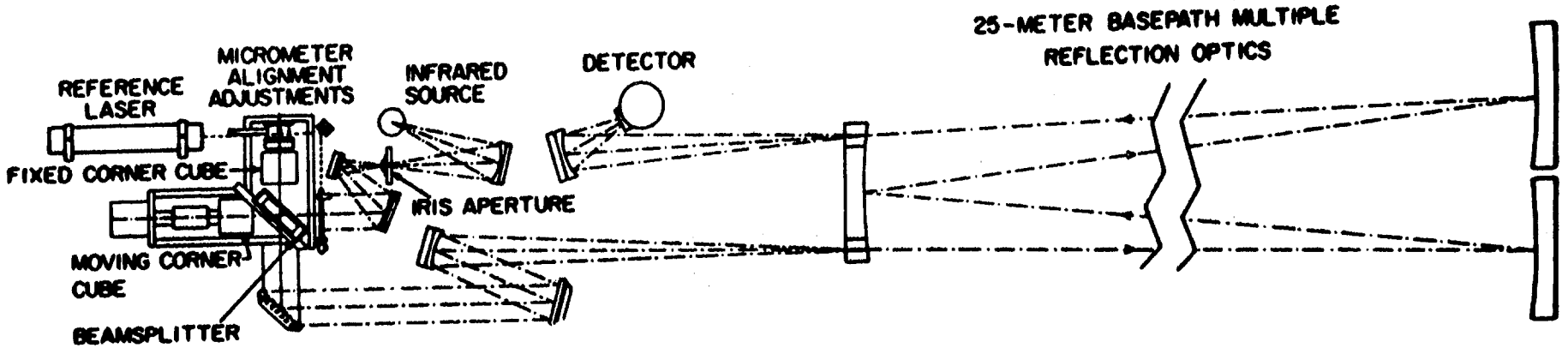


Figure V-2. Schematic optical diagram of the longpath FT-IR spectrometer.

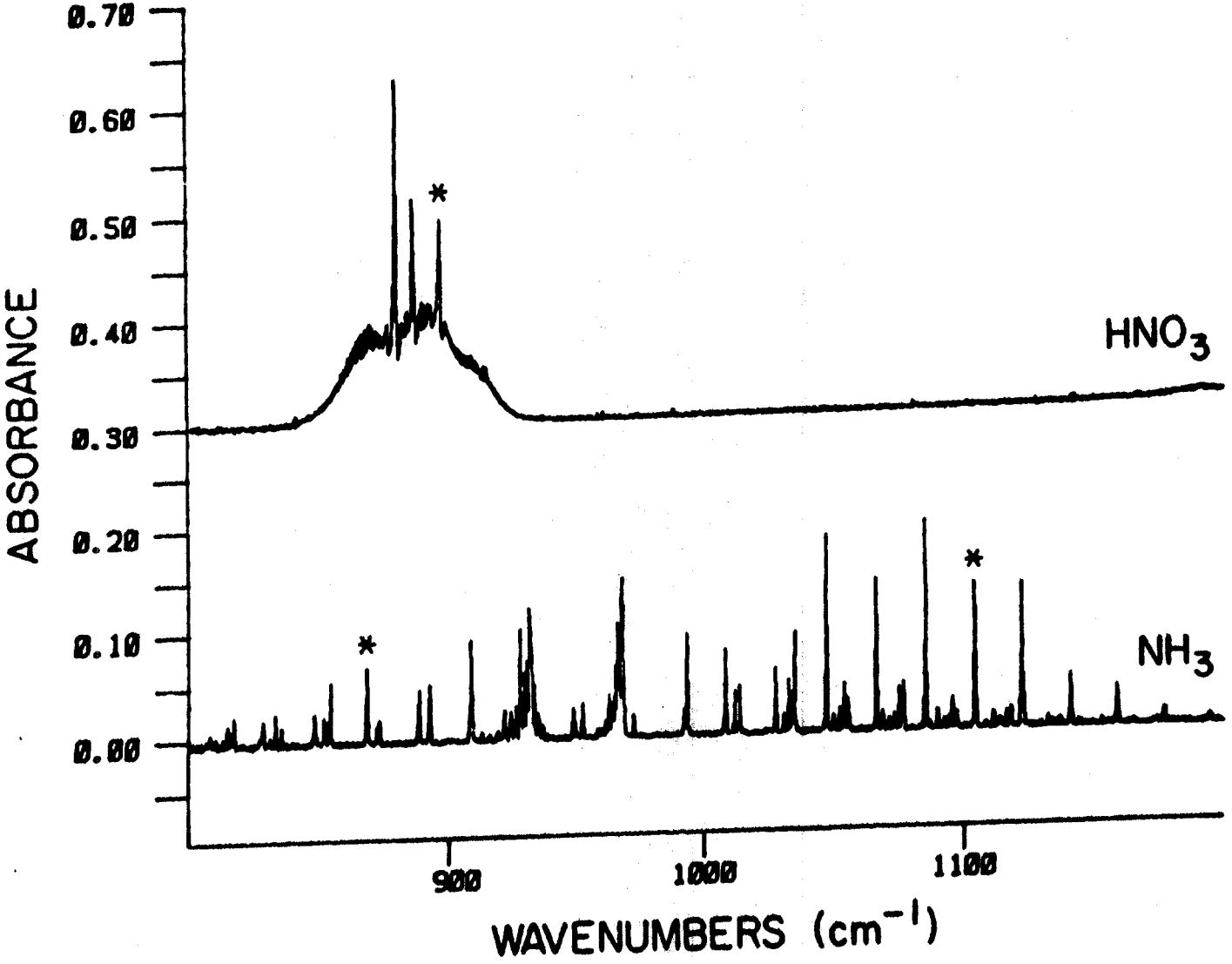


Figure V-3. Reference spectra of gaseous HNO_3 (0.61 torr) and NH_3 (0.23 torr) at spectral resolution of 0.125 cm^{-1}, pathlength of 25 cm, total pressure with N_2 of 740 torr. The HNO_3 plot is offset by 0.30 absorbance (base 10) unit for clarity. Asterisks mark the absorption peaks used for analysis.

expanded plot of the HNO_3 spectrum in the range 870-910 cm^{-1} is presented in Figure V-4, to which is added a qualitative single beam spectrum of "clean" ambient air at a pathlength of 1150 m. The Q-branch at 896.1 cm^{-1} was the most appropriate one for quantitative measurement because of its favorable half-width and minimal interference by atmospheric water vapor. We restricted our measurements to the heights of the sharp absorption (Q-branch) features only, since measurements which include the broad underlying envelope were more susceptible to unknown interferences. The 885.4 cm^{-1} Q-branch was totally free of interferences but its relatively narrower line shape was more susceptible to distortion by noise, while the strongest Q-branch at 878.9 cm^{-1} was severely overlapped by a strong water line.

Of the numerous sharp features of the NH_3 spectrum depicted in Figure V-3, the lines at 1103.4 and 867.9 cm^{-1}, though not the strongest, suffer the least interference by H_2O and CO_2 absorption lines and were therefore the ones chosen for analysis. The line positions of NH_3 relative to those of atmospheric H_2O (and CO_2) in the 1080-1120 cm^{-1} region are shown in Figure V-5. The calibration procedure for NH_3 was straightforward. Spectra were recorded at 0.125 cm^{-1} resolution for several NH_3 pressures in the range 0.2-1 torr, which were measured to within ±0.005 torr accuracy with an MKS Baratron capacitance manometer. The NH_3 samples were transferred to a 25-cm cell with KBr windows and pressurized with N_2 gas to atmospheric pressure. No measurable decay of NH_3 concentration was observed within the 15-minute period during which repeat spectra were recorded for each sample. These data yielded absorptivities (base 10) at 23°C and 740 torr total pressure of 18.2 cm^{-1} atm^{-1} for the 1103.4 cm^{-1} peak and 9.7 cm^{-1} atm^{-1} for the 867.9 cm^{-1} peak, with uncertainties of ±5% (two standard deviations) for both values.

A similar calibration procedure was not possible for HNO_3 because of its significant decay to the walls of the 25-cm cell. We determined our high resolution absorptivity values relative to the data of Graham and Johnston (1978), who made an accurate determination of the absorptivity of the HNO_3 ν_4 (1325 cm^{-1}) fundamental band at ~2 cm^{-1} resolution using two independent methods for generating HNO_3 (for more details see also Graham 1975). We assigned Graham and Johnston's (1978) absorptivity value

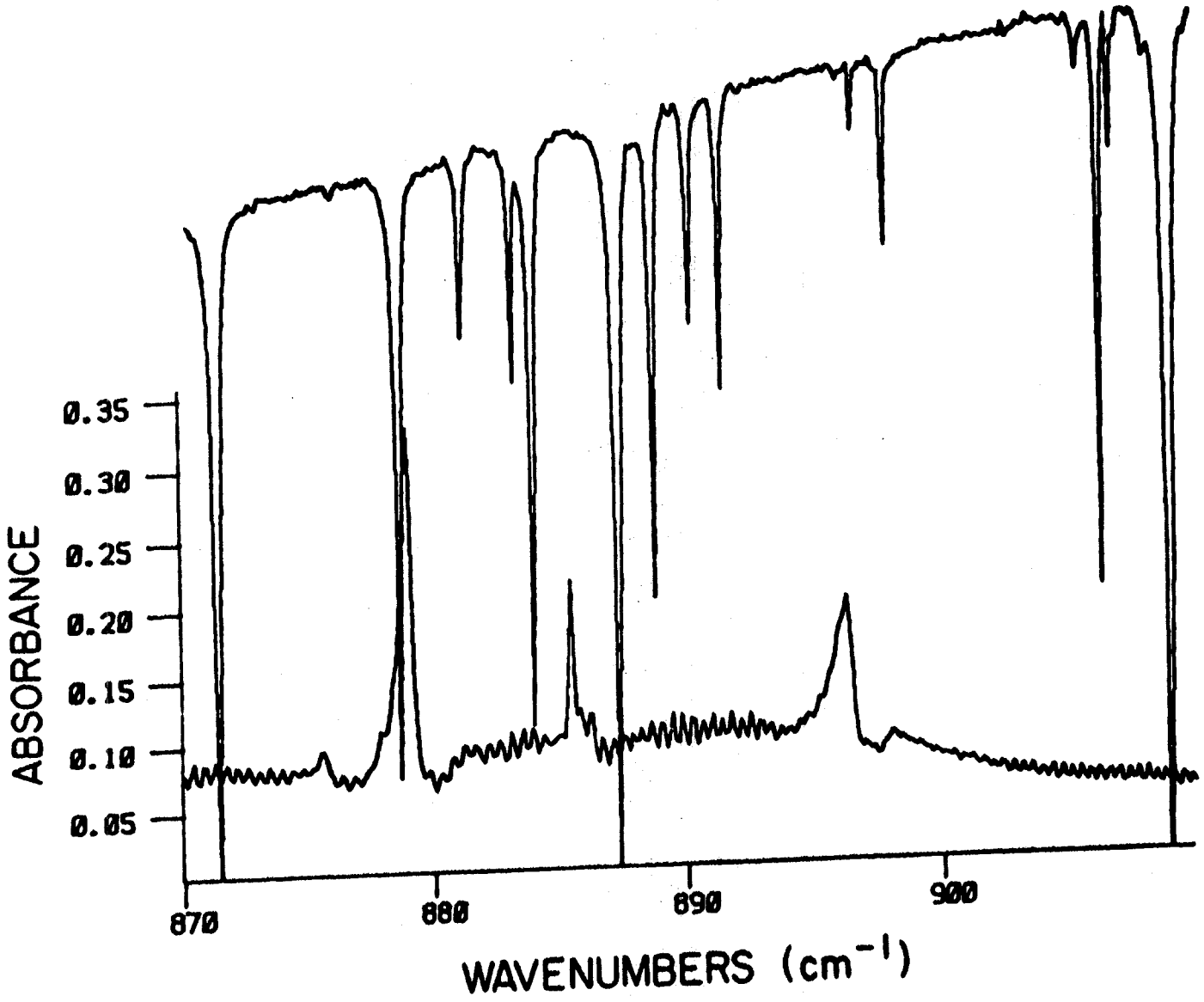


Figure V-4. Infrared absorption peaks of HNO_3 (lower trace) relative to atmospheric H_2O absorptions (upper trace) in the 870-910 cm^{-1} region.

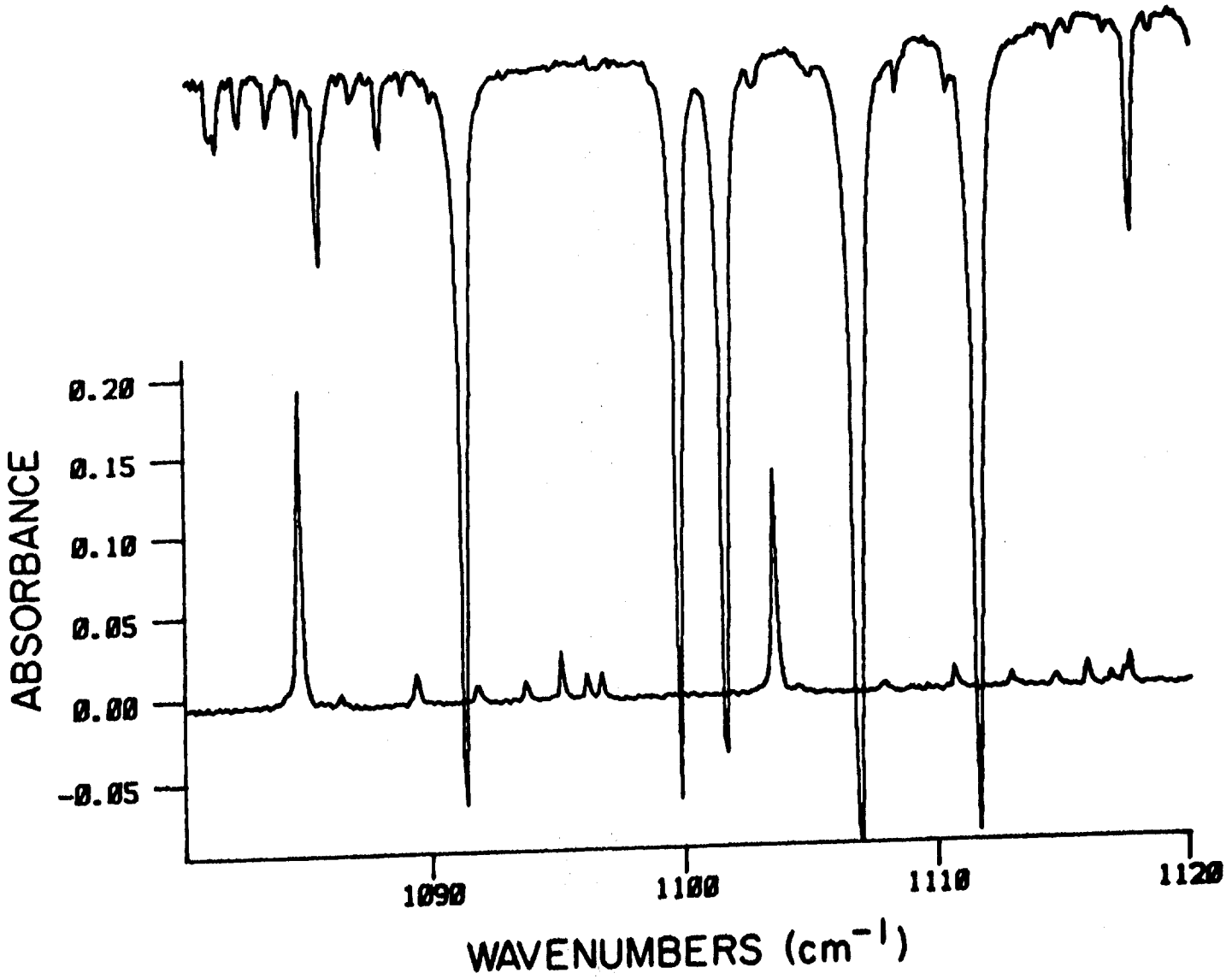


Figure V-5. Infrared absorption peaks of NH_3 (lower trace) relative to atmospheric H_2O and CO_2 absorptions (upper trace) in the 1080-1120 cm^{-1} region.

(peak-to-baseline) for the broad ν_4 P-branch at 1315 cm^{-1} to the same feature in our 0.125 cm^{-1} resolution spectrum after smoothing the latter to ~2 cm^{-1} resolution. The absorptivity for a Q-branch (e.g., 896.1 cm^{-1}) at 0.125 cm^{-1} resolution was then determined from the intensity ratio of the unsmoothed Q-branch to the smoothed P-branch.

Smoothing removes the fine structure superimposed on the ν_4 band envelope, and in order to test the adequacy of the smoothing function employed, measurements were carried out in which 2 cm^{-1} and 0.125 cm^{-1} resolution spectra were recorded alternately for an HNO_3 sample. To take into account the HNO_3 decay in the cell, the 1315 cm^{-1} peak heights at 2 cm^{-1} resolution were plotted against time, as were those of the 0.125 cm^{-1} resolution spectra after having been smoothed to ~2 cm^{-1} resolution. The two curves were found to be indistinguishable, indicating the accuracy of the smoothing function applied. The above procedure yielded a value of 5.2 ± 0.4 cm^{-1} atm^{-1} for the absorptivity (base 10) of the HNO_3 peak at 896.1 cm^{-1} (Q-branch height only) with the two standard deviation error including that reported by Graham (1975). This value is in fact the same as that we previously determined for this peak at 0.5 cm^{-1} resolution (Tuazon et al. 1980). Following the same method, the absorptivity of the 885.4 cm^{-1} Q-branch was found to be 6.1 ± 0.5 cm^{-1} atm^{-1}.

The calibration procedure for HCHO was the same as that for NH_3. Formaldehyde samples were pre-distilled from paraformaldehyde and immediately used after collection in a liquid nitrogen cooled trap. The absorptivity value of the 2781.0 cm^{-1} Q-branch, an absorption peak well isolated from H_2O absorptions, was determined to be 8.9 ± 0.5 cm^{-1} atm^{-1}.

4. Treatment of Data

The quantitative analysis of species such as NH_3, which possess relatively narrow Q-branch features which are sufficiently resolved from atmospheric H_2O absorptions, was normally straightforward. The absorbance ($\log I_o/I$) was derived directly from the single beam spectrum, and thus a ratio plot against an actual background spectrum was not necessary. Provided that the detector had a linear response, I_o and I as determined from a single beam spectrum had values on an arbitrary scale in which zero corresponded to zero signal on the detector. The appropriate differential absorption coefficient, such as those determined above, and the absorption pathlength had to be applied to the absorption intensity measured between

I_o and I in order to convert to concentration units. This procedure was followed for the 1103.4 and 867.9 cm^{-1} lines of NH_3.

Estimates of the HNO_3 concentration could also be obtained from single-beam spectra by employing the 885.4 cm^{-1} Q-branch. However, the HNO_3 analysis was more reliably carried out using the 896.1 cm^{-1} Q-branch by ratioing the sample spectrum with a clean background spectrum, a procedure which improved the baseline and resulted in essentially complete cancellation of a very weak H_2O interference. Background spectra were chosen from those recorded at around midnight during low pollution days, since previous measurements (Spicer et al. 1982) showed HNO_3 levels that were much lower (<1 ppb) than the FT-IR detection limit under these conditions.

The peak-to-peak noise level in the ratio spectrum was typically 0.0025 absorbance unit (base 10), corresponding to a 250:1 signal to peak-to-peak noise ratio for single spectral records. The absorption peaks used for the analyses were much wider than the frequency of random noise, such that peak heights as small as the noise level could be detected above the noise itself. Thus, the detection sensitivities were 3-5 ppb for HNO_3, 1-2 ppb for NH_3 and 2-3 ppb for HCHO. The lower detection limit for each compound was realized when turbulence due to temperature gradients and/or wind were minimal (for example, during nighttime hours).

The possible detection of N_2O_5 depended on how well its broad band, centered at 1246 cm^{-1} (ν_{12}), could be discerned from interfering H_2O absorptions. The H_2O interferences were reduced by ratioing the sample spectra against selected "background" spectra taken during those periods (mid-morning to noon) when N_2O_5 was believed not to be present due to the rapid photolysis of NO_3 radicals. Although exact cancellation of the H_2O absorptions was not possible, the "windows" between these absorptions were sufficient to define a baseline from which the presence of a broad absorption contour could be distinguished. From the literature value of 18.8 cm^{-1} atm^{-1} for the absorptivity of the 1246 cm^{-1} peak (Graham 1975, Graham and Johnston 1978), it was calculated that 5 ppb N_2O_5 at a pathlength of 1150 m would give a signal of ~0.01 absorbance unit (base 10), approximately 4 times the peak-to-peak baseline noise of the ratio spectrum.

The largest source of uncertainty in the analyses was the noise level in the spectrum, with other errors being generally negligible. We assigned to each peak height measurement the maximum error, which was equal to the peak-to-peak noise level. For HNO_3 this error was ±4 ppb. The uncertainty arising from the error in the absorptivity (of the 896.1 cm^{-1} Q-branch in this case) increased with the concentration. However, this contribution to the overall error limit was relatively small for the range of HNO_3 concentrations encountered. For example, it increased the ±4 ppb error by only 10% when included in the error calculation for an HNO_3 concentration of 25 ppb.

For NH_3 concentrations $\leq$20 ppb, the sum of uncertainties due to noise and error in the absorptivity of the 1103.4 cm^{-1} line was ±1.5 ppb. At higher concentrations the contribution from the absorptivity error became relatively more important. A detailed plot of this error contribution as a function of concentration revealed that it is nearly linear in the concentration range 20 to 100 ppb, permitting the additional error to be calculated from the empirical formula $(0.044)([NH_3]-20)$ ppb. Thus, for the measurement of 60 ppb NH_3, the total error can be calculated as $[1.5 + (0.044)(60-20)] = \pm 3.3$ ppb.

For the range of HCHO concentrations encountered in the 1986 Glendora study, the measurement errors were less than ±3 ppb.

C. Results and Discussion

As discussed in Section II, our measurements were conducted in conjunction with the CARB-sponsored Carbonaceous Species Methods Comparison Study which occurred from 0800 PDT, August 12, to 0800 PDT, August 21, 1986. In contrast with the low level of air pollution during the 1985 Claremont summer field study, this August 1986 measurement period at Citrus College was characterized by moderately high levels of photochemical activity. Except for the second day of measurements, the maximum hourly average O_3 concentrations exceeded 200 ppb each day.

The FT-IR spectra obtained were analyzed for the simultaneous concentrations of HNO_3, NH_3 and HCHO. The detailed instantaneous data are presented in Table V-1 and are plotted in Figure V-6. The hourly average concentrations are presented in Tables V-2 to V-4. Except for periods of power disruption on August 14 and the loss of most of the daytime data on

Table V-1. Simultaneous HNO_3, NH_3, and HCHO Concentrations (ppb) in Glendora, CA, August 12-21, 1986 by Long Pathlength FT-IR Spectroscopy. (No entries for HNO_3 mean below detection limit. Asterisks mark the times where gaps in the data occur)

PDT	HNO_3	NH_3
8/12/86		
0758		13.1
0811		8.1
0825		7.4
0837		10.3
0851	2.1	8.1
0905	2.1	6.9
0917	2.6	6.7
0930	3.9	6.1
0944	3.9	5.3
0957	4.5	6.1
1010	4.4	4.9
1024	5.3	3.3
1037	8.9	3.9
1052	9.7	2.9
1119	11.8	2.6
1136	14.4	3.9
1149	14.5	4.2
1202	15.2	3.5
1221	15.3	3.4
1234	16.3	3.7
1250	16.3	4.6
1305	17.7	4.7
1320	15.8	4.7
1339	19.5	5.0
1353	20.0	2.9
1406	20.6	3.5
1419	21.6	4.3
1433	23.7	4.2
1447	22.2	3.9
1503	21.5	3.5
1517	21.6	2.8
1532	18.9	4.7
1546	18.7	3.8
1608	13.9	3.4
1622	12.4	3.0
1635	10.5	3.4
1651	11.6	3.1
1705	5.8	3.2
1718	5.7	3.2
1732	6.7	2.9
1745	5.9	3.1
1802	5.9	3.4
1816	4.6	4.1
1828	4.0	5.9
1848	5.4	5.6
1904	4.8	6.3
1920	3.5	6.2
1934	2.8	5.0
1947	2.6	6.1
2000	2.6	6.0
2014		4.0
2106		4.5
2118		4.6
2132		5.1
2144		5.1
2201		4.7
2215		4.6
8/13/86		
0027		5.7
0043		5.1
0059		5.3
0114		5.0
0130		5.2
0146		5.0
0201		5.5
0217		5.5
0233		5.5
0249		5.1
0304		4.6
0320		4.3
0336		4.2
0351		5.2
0407		4.7
0423		4.7
0439		4.6
0454		6.7
0510		5.1
0526		4.9
0541		4.4
0557		5.3
0612		4.6
0628		5.0
0644		4.5
0659		5.4

HCHO
4.8
5.1
4.3
5.4
5.1
5.1
5.4
4.6
5.9
5.3
4.0
3.6
4.3
4.0
3.9
4.5
4.0
4.6
5.5
5.5
4.2
4.4
3.9
4.3
5.2

Table V-1 (continued) - 2

PDT	HNO_3	NH_3	HCHO
0715		6.6	6.2
0731		5.9	7.0
0746		7.4	9.7
0802		6.1	9.0
0818		5.8	9.0
0833		4.9	7.9
0849		4.8	10.3
0904	1.7	2.2	10.7
0920	1.7	1.8	12.5
0936	3.8	1.8	12.6
0951	4.3	1.9	13.4
1007	4.5	1.7	13.5
1035	7.6	1.4	12.5
1048	8.0	1.8	13.7
1101	8.7	1.7	12.6
1114	8.7	2.2	12.2
1128	11.8	1.8	12.7
1145	10.7	1.9	11.3
1158	12.5	1.8	10.6
1211	12.6	1.9	11.4
1229	12.9	3.0	12.0
1248	14.0	3.0	10.9
1309	15.5	3.0	9.7
1331	13.9	2.8	10.6
1344	15.9	3.6	11.9
1357	14.8	3.2	10.1
1410	15.5	3.6	12.3
1423	13.4	3.5	11.6
1440	16.6	3.8	11.2
1453	16.9	3.1	11.1
1506	17.9	3.1	11.3
1522	19.7	3.9	12.1
1535	18.1	4.0	10.3
1548	17.3	3.9	12.4
1601	16.5	4.1	15.3
1614	18.5	4.5	13.9
1630	13.0	4.8	13.0
1643	13.9	3.9	12.7
1655	12.9	3.9	12.1
1706	13.4	3.7	13.1
1718	13.5	3.9	13.1
1734	13.0	3.5	10.9
1747	10.4	4.2	12.6
1800	10.6	4.0	9.8
1813	9.7	4.1	11.6
1827	8.3	4.1	9.0
1850	6.0	4.1	10.1
1913	4.3	3.8	8.3
1926	5.4	4.5	7.9
1939	5.2	4.1	8.1
1952	4.5	3.6	9.1
2005	4.4	3.4	7.5
2018	3.4	3.7	7.9
2034	5.1	3.7	7.1
2113	2.4	3.7	6.2
2133		5.9	6.7
2146		6.4	6.3
2206		6.8	5.9
2226		4.3	7.6
2245		3.9	6.9
2305		4.6	7.4
2324		4.2	5.0
2344		3.8	6.5
<u>8/14/86</u>			
0004		3.7	4.8
0023		2.6	5.5
0043		2.7	6.2
0102		2.9	5.9
0122		3.6	5.0
0142		3.7	4.3
0201		4.7	4.7
0221		3.5	3.7
0241		3.4	4.2
0300		3.0	4.5
0320		2.6	4.2
0339		1.9	3.6
0359		2.4	4.0
0419		2.7	4.5
0438		3.0	5.0
0458		2.5	4.9
0518		2.9	4.5
0537		4.0	3.4
0557		4.1	3.3
0616		3.4	3.4
0636		2.8	3.8
0656		2.5	6.0
0716		2.4	6.2
0735		2.1	5.7
0755		1.5	7.4
0815		2.6	8.2
0834		1.8	10.9
0854	2.6	1.5	12.2
*0914	2.6	1.4	12.5
*1033	5.1	1.7	12.8

Table V-1 (continued) - 3

PDT	HNO_3	NH_3	HCHO
*1059	8.2	1.5	14.6
*1153	10.4	2.4	11.8
1208	12.8	2.7	12.1
1221	14.5	2.6	9.1
1240	16.1	2.4	13.7
1253	16.1	3.3	13.3
1309	15.7	2.9	13.0
*1322	17.5	3.2	12.5
*1507	20.1	2.7	9.4
1520	22.3	3.0	15.3
1531	24.6	2.3	17.4
1543	22.2	2.9	18.7
1555	23.1	2.3	19.9
1606	22.2	2.0	16.8
1620	19.6	3.1	15.3
1643	17.5	1.9	13.2
1655	18.2	2.2	12.7
1711	18.8	1.7	13.3
1723	18.1	1.2	12.6
1735	17.1	1.6	12.4
1746	16.3	2.1	13.5
1801	15.9	2.0	10.9
1818	13.8	1.6	10.8
1830	12.8	2.2	10.9
1842	13.0	2.2	12.8
1853	11.5	1.5	11.6
1925	10.2	2.0	10.3
1938	8.1	1.4	9.5
1951	8.4	2.2	8.4
2004	8.7	1.4	9.5
2017	5.6	1.8	8.5
2030	5.3	2.0	8.3
2044	3.4	2.3	7.6
2057	3.8	1.7	7.2
2110	2.1	2.0	7.7
2123		2.1	6.0
2136		2.1	6.0
2210		1.5	4.7
2229		1.7	5.5
2249		1.5	5.3
2309		1.5	4.9
2328		2.6	4.2
2348		2.3	3.6
8/15/86			
0008		2.5	4.1
0027		2.8	3.4
0047		2.5	3.8
0107		2.8	3.6
0126		2.5	3.4
0146		3.4	3.1
0206		3.1	2.7
0225		2.8	2.2
0245		3.6	3.0
0305		3.2	3.9
0324		3.8	2.6
0344		3.2	2.8
0404		3.3	3.9
0424		4.4	3.5
0443		3.9	3.6
0503		4.2	3.1
0523		5.2	2.9
0543		4.9	3.8
0602		3.5	4.0
0622		3.4	4.9
0641		4.0	4.4
0701		4.7	4.2
0721		2.9	4.2
0741		2.0	4.3
0800		4.2	4.6
0820		1.3	6.1
0840		1.3	7.4
0859	1.7	1.6	7.3
0919	3.1	1.1	8.8
1016	6.2	0.7	10.5
1029	8.4	1.3	10.7
1043	9.9	1.2	10.3
1100	11.3	1.4	10.1
1112	9.7	1.2	10.8
1126	13.5	1.3	11.3
1138	12.8	1.3	12.4
1151	13.1	1.8	12.8
1203	14.5	1.4	12.2
1219	17.1	1.4	12.8
1231	16.0	1.9	11.7
1244	17.1	1.2	11.0
1256	21.4	2.1	11.1
1309	21.2	1.7	11.1
1325	20.9	2.1	12.2
1341	19.6	3.0	10.4
1353	20.2	2.4	13.1
1410	25.0	2.7	13.1
1425	22.6	3.5	17.8
1440	22.2	2.9	17.6
1453	21.6	3.3	16.4

Table V-1 (continued) - 4

PDT	HNO_3	NH_3	HCHO
1505	21.4	3.1	16.2
1518	19.6	2.7	15.1
1530	21.4	2.5	14.3
1542	20.5	2.5	15.8
1604	17.1	2.3	12.9
1616	16.2	2.3	13.8
1629	16.2	2.8	12.2
1641	11.5	2.1	13.5
1653	10.9	1.9	13.8
1707	10.8	2.0	12.5
1720	10.5	1.4	9.1
1732	9.4	2.1	6.1
1744	9.0	2.3	7.9
1757	9.4	2.7	9.1
1830	8.2	1.6	7.7
1842	6.7	2.2	9.0
1854	6.8	1.8	10.6
1907	6.8	1.9	8.8
1919	4.3	2.1	8.1
1938	2.9	2.8	8.1
1950	2.6	2.3	6.8
2003	2.2	2.7	7.2
2015		2.7	7.4
2027		3.6	5.5
2106		3.6	5.4
2125		2.9	6.0
2145		2.9	3.4
2205		2.7	3.4
2224		3.1	2.7
2244		3.0	4.4
2323		3.2	5.7
2343		4.8	4.4
8/16/86			
0003		3.1	5.5
0022		3.1	4.0
0042		3.6	4.3
0101		3.2	4.9
0121		4.0	4.9
0141		3.5	4.9
0200		3.6	4.5
0220		3.2	5.1
0240		3.2	4.8
0259		4.2	4.0
0319		3.1	4.7
0339		5.1	3.7
0359		3.8	4.9
0418		3.6	4.2
0438		3.3	4.9
0458		3.6	4.7
0517		3.8	3.2
0537		3.4	4.3
0557		2.7	4.4
0616		2.6	4.0
0636		3.8	3.1
0656		3.3	4.4
0715		2.8	5.0
0735		1.8	5.7
0755	0.9	1.3	7.9
0815	3.0	1.6	9.8
0834	2.1	1.5	10.0
0854	4.1	0.6	9.7
0914	3.8	1.1	11.2
0933	3.8	1.1	11.2
1015	8.1	1.5	12.2
1028	8.7	0.9	12.6
1048	10.3	0.9	14.4
1100	11.6	1.8	14.9
1118	13.8	1.8	14.9
1131	13.7	2.3	16.1
1143	15.5	1.5	12.6
1155	15.8	2.0	13.8
1207	15.6	2.2	12.4
1219	16.0	2.2	12.3
1231	14.4	2.9	11.3
1243	15.5	2.2	11.8
1255	17.7	2.4	10.3
1308	17.5	2.3	10.1
1320	17.1	2.8	9.6
1332	19.2	2.3	9.6
1344	16.6	3.1	11.4
1356	19.7	2.8	9.9
1409	19.4	2.8	10.9
1421	20.8	3.2	10.5
1433	20.3	2.8	10.9
1445	20.3	3.1	11.7
1457	21.1	3.5	14.2
1509	20.8	3.1	14.1
1522	20.5	3.3	13.8
1534	20.5	2.6	16.7
1546	20.5	2.6	14.3
1558	22.8	2.6	15.5
1610	19.8	3.5	13.8
1623	20.5	3.1	15.2
1635	19.1	3.1	13.9

Table V-1 (continued) - 5

PDT	HNO_3	NH_3	HCHO
1647	20.9	2.2	14.4
1659	21.6	2.9	12.7
1711	19.9	2.3	11.6
1724	20.9	2.1	13.5
1736	19.6	2.7	14.7
1748	16.9	2.4	13.4
1800	18.7	2.6	12.6
1812	13.1	2.3	12.1
1902	10.3	2.3	9.2
1917	7.9	2.8	9.3
1924	6.7	2.7	9.1
1942	8.2	3.1	8.9
1954	6.8	3.2	8.9
2006	5.3	4.7	9.1
2024	5.4	4.8	8.2
2036	5.1	3.8	8.1
2049	2.6	5.0	9.5
2144		4.5	7.6
2152		3.9	9.0
2212		3.6	8.0
2232		3.8	7.7
2251		3.6	6.8
2311		3.7	5.3
2331		4.3	4.7
2350		3.8	5.9
8/17/86			
0010		3.7	5.6
0030		4.0	6.9
0049		4.1	6.2
0109		3.2	7.4
0129		5.1	7.9
0148		3.4	6.2
0208		3.4	6.6
0228		3.7	6.9
0248		4.0	6.3
0307		2.9	8.9
0327		2.1	7.5
0347		2.7	5.8
0406		2.6	8.2
0426		1.8	7.8
0446		2.5	6.3
0506		2.1	7.9
0525		1.8	8.3
0545		2.6	7.1
0605		2.1	5.2
0624		2.8	6.9
0644		2.0	6.2
0704		2.2	7.0
0723		3.4	6.3
0743		1.7	7.4
0803		2.2	8.5
0823		3.8	8.3
0843		4.2	10.4
0902		5.3	11.7
0922		5.4	13.1
0942		5.5	18.5
*1002		5.6	18.9
*2235		5.9	6.0
2253		4.2	6.2
2306		3.5	5.3
2317		4.6	6.0
2337		3.3	6.3
2356		4.0	6.4
8/18/86			
0016		5.0	6.9
0036		5.9	5.5
0056		8.3	7.2
0115		3.8	8.1
0135		3.9	6.9
0155		5.2	8.7
0214		5.9	7.2
0234		5.3	7.9
0254		7.5	7.4
0313		6.5	7.7
0333		6.2	7.9
0353		6.0	7.3
0412		5.6	7.5
0432		5.8	8.1
0452		6.7	7.7
0511		4.6	7.9
0531		4.8	8.0
0550		4.3	6.5
0610		4.4	5.6
0630		4.2	6.0
0649		4.7	6.4
0709		6.2	9.3
0729		4.1	7.9
0748	2.8	4.6	8.4
0808	2.7	4.3	8.9
0828	3.1	4.6	9.9
0847	3.7	7.5	9.2

Table V-1 (continued) - 6

PDT	HNO_3	NH_3	HCHO
0907	5.6	8.2	15.0
0926	5.5	7.1	15.8
0946	5.6	5.7	10.5
1004	9.9	8.4	15.3
1017	11.2	9.4	17.0
1029	10.3	9.7	15.3
1057	12.3	11.5	21.5
1111	12.8	14.3	22.0
1123	13.1	14.5	20.5
1140	15.0	12.8	22.4
1156	15.5	11.5	18.8
1207	20.7	9.8	22.2
1220	19.2	9.0	19.3
1233	20.7	6.2	15.2
1245	15.4	5.5	12.4
1256	23.9	10.4	13.6
1308	20.7	10.1	14.6
1320	17.7	7.0	10.3
1333	15.4	5.0	9.3
1345	15.9	4.7	9.1
1357	13.7	3.8	8.2
1409	16.7	4.3	10.6
1421	16.7	4.1	8.9
1433	18.5	4.6	13.2
1445	18.5	4.2	11.6
1451	15.7	4.6	11.7
1509	22.4	6.2	14.4
1521	19.5	4.7	14.5
1534	27.7	6.2	15.1
1546	26.2	6.1	19.1
1558	26.2	5.8	16.3
1610	21.2	5.3	15.1
1622	21.3	4.8	14.1
1635	16.1	5.6	14.6
1647	17.2	6.1	17.9
1700	16.4	5.4	12.4
1712	16.3	5.7	11.8
1724	15.0	4.4	12.3
1737	15.2	6.1	10.4
1750	13.0	5.4	11.9
1802	12.8	5.5	10.8
1814	13.1	5.0	9.6
1826	9.9	6.9	9.7
1839	5.7	6.6	10.0
1852	5.4	8.1	6.9
1932	2.8	5.3	7.1
1944	2.8	4.3	4.7
1956	2.5	4.8	5.8
2009	2.2	4.7	4.8
2021		6.8	6.7
2035		7.9	8.6
2047		8.7	8.1
2059		8.2	7.1
2111		9.4	5.4
2124		9.0	5.8
2206		6.9	7.2
2226		7.6	7.8
2246		9.5	8.5
2305		8.5	8.0
2325		7.7	8.5
2345		7.1	7.8
8/19/86			
0004		5.9	9.1
0024		5.9	6.9
0044		10.5	7.6
0103		6.9	7.7
0123		5.3	6.2
0143		6.9	5.6
0202		7.5	6.7
0222		9.6	6.0
0242		8.0	7.5
0301		6.7	7.9
0321		5.3	6.1
0341		8.5	7.9
0400		10.2	8.4
0420		7.1	8.1
0439		6.1	7.7
0459		8.9	8.3
0519		7.8	6.4
0538		4.2	6.5
0558		7.3	7.9
0618		6.4	9.0
0637		6.4	10.0
0657		8.5	11.1
0717		5.8	11.2
0737	2.6	5.9	14.3
0757	2.6	6.0	14.6
0816	4.9	6.3	14.2
0836	6.0	6.1	14.9
0855	6.7	7.9	14.2
0915	8.4	6.8	12.7
0935	11.5	6.5	15.5
1006	16.2	6.6	13.8
1018	16.1	5.7	13.4

Table V-1 (continued) - 7

PDT	HNO_3	NH_3	HCHO
1030	17.3	6.0	14.3
1043	17.3	6.4	15.2
1057	18.1	7.0	15.3
1109	21.9	6.9	18.6
1121	17.5	6.9	15.9
1133	19.5	6.9	11.5
1148	20.6	8.7	13.4
1200	22.9	6.4	11.5
1213	18.2	5.4	13.7
1225	21.6	5.5	14.2
1237	22.3	4.9	13.8
1249	12.5	3.9	9.2
1305	13.4	3.2	8.7
1317	16.6	5.8	10.8
1329	22.4	6.6	12.2
1346	29.2	7.1	19.0
1355	33.1	8.1	23.8
1405	27.2	7.8	21.3
1415	27.3	6.5	16.5
1426	23.4	6.4	13.3
1436	22.3	6.1	13.0
1448	21.2	5.8	12.7
1501	20.0	5.1	11.9
1512	18.5	5.7	10.6
1522	17.2	5.1	13.3
1532	16.6	4.5	10.9
1542	12.5	6.4	9.4
1554	11.6	4.7	9.0
1604	10.7	4.2	6.8
1614	8.3	4.7	7.6
1624	7.5	4.3	8.2
1634	7.1	4.9	6.7
1645	7.6	4.4	8.1
1655	6.2	5.2	7.0
1705	4.8	5.1	7.6
1720	6.5	5.3	8.1
1733	6.8	5.1	8.3
1747	7.4	5.1	8.8
1759	7.2	7.1	7.4
1811	4.7	5.1	7.6
1823	3.7	6.0	6.2
1835	5.0	6.8	6.7
1847	5.0	5.8	7.2
1902	4.6	8.1	7.6
1914	4.0	7.0	6.6
1927	3.3	6.9	7.2
1939	3.4	7.1	7.1
2007	3.3	9.1	8.5
2017	2.7	8.1	8.1
2029		11.0	7.7
2042		9.5	7.0
2054		7.2	7.7
2106		7.1	6.3
2118		7.7	7.2
2130		7.0	7.1
2142		6.5	7.8
2155		6.0	5.9
2207		6.7	6.8
2219		7.2	9.3
2231		7.5	9.9
2243		7.0	8.7
2314		6.9	8.1
2334		5.8	8.6
2353		6.0	9.1
8/20/86			
0013		5.0	8.4
0032		5.8	9.6
0052		5.7	8.5
0112		5.6	8.4
0131		6.9	8.2
0151		5.8	8.8
0210		6.4	8.8
0230		5.7	9.0
0250		5.4	8.2
0309		5.8	7.1
0329		6.0	9.6
0348		6.1	9.2
0408		6.0	8.9
0428		6.9	8.0
0447		7.8	8.4
0507		5.9	8.8
0527		5.6	8.6
0546		5.8	10.1
0606		6.1	10.0
0625		6.3	11.0
0645		6.5	10.3
0705		6.4	10.4
0724		7.1	10.7
0744		7.2	13.0
0803	2.3	9.5	13.9
0823	3.7	11.5	18.0
0843	3.8	9.3	23.9
0902	5.0	8.3	22.2
0923	5.6	9.8	18.9

Table V-1 (continued) - 8

PDT	HNO_3	NH_3	HCHO
0942	6.4	11.2	25.2
1001	6.5	10.0	25.1
1013	9.2	9.4	23.5
1025	10.4	9.9	23.3
1038	10.0	7.5	16.9
1050	12.1	8.8	18.5
1104	14.1	8.9	16.9
1117	14.5	8.8	17.6
1129	17.5	9.6	14.7
1141	18.3	8.9	16.4
1153	17.5	8.1	13.4
1208	18.7	9.5	17.4
1220	23.4	8.7	18.9
1232	22.0	7.1	20.5
1244	24.9	7.5	21.4
1300	24.5	6.3	17.7
1311	21.7	6.5	19.3
1321	20.1	6.3	17.9
1331	19.6	6.6	15.4
1341	22.0	6.2	14.7
1352	21.0	5.9	17.5
1402	20.0	5.5	18.4
1414	20.0	5.0	16.8
1424	21.8	4.9	16.7
1434	19.0	6.3	16.7
1444	18.0	6.4	16.1
1454	15.8	7.9	11.1
1507	15.4	7.0	13.1
1517	14.8	6.3	12.3
1530	14.3	6.3	11.9
1540	14.3	5.1	11.9
1550	15.0	6.1	12.8
1600	15.7	5.9	10.4
1610	12.8	5.1	9.9
1621	8.5	5.4	8.8
1631	7.9	5.0	8.0
1643	7.3	4.6	7.1
1656	5.0	4.3	5.2
1706	5.7	5.0	6.4
1716	6.3	5.7	7.6
1727	6.5	5.2	6.8
1737	6.0	5.4	8.4
1747	6.3	5.7	8.0
1757	6.7	6.0	9.0
1807	9.1	5.9	10.2
1817	9.0	7.6	11.3
1828	7.5	6.4	11.3
1839	7.1	8.7	11.4
1849	4.2	8.1	12.1
1900	5.8	9.3	9.8
1910	5.7	10.4	12.4
1920	4.1	9.8	11.7
1930	3.4	10.3	11.1
1940	4.6	9.8	9.1
2023	5.8	6.6	9.1
2035	4.3	6.1	10.4
2050	3.3	8.9	8.4
2110	3.7	6.3	8.7
2129	1.2	5.9	7.6
2149		8.3	9.7
2209		9.9	8.4
2228		8.2	7.8
2248		5.6	8.3
2307		10.8	8.5
2327		9.1	8.6
2347		6.7	9.7
8/21/86			
0006		5.1	10.5
0026		6.2	9.8
0046		6.5	10.6
0106		6.0	11.8
0125		5.5	9.2
0145		7.5	10.1
0204		8.3	9.4
0224		7.5	9.3
0244		7.2	8.6
0303		6.7	9.3
0323		6.1	7.9
0343		8.1	10.8
0402		7.9	8.5
0422		6.8	8.4
0442		7.0	8.4
0501		6.8	8.5
0521		7.1	10.5
0541		5.8	9.6
0601		6.6	10.1
0620		6.1	10.5
0640		6.5	9.0
0700		6.3	11.6
0717		6.1	13.0
0730		7.0	14.3

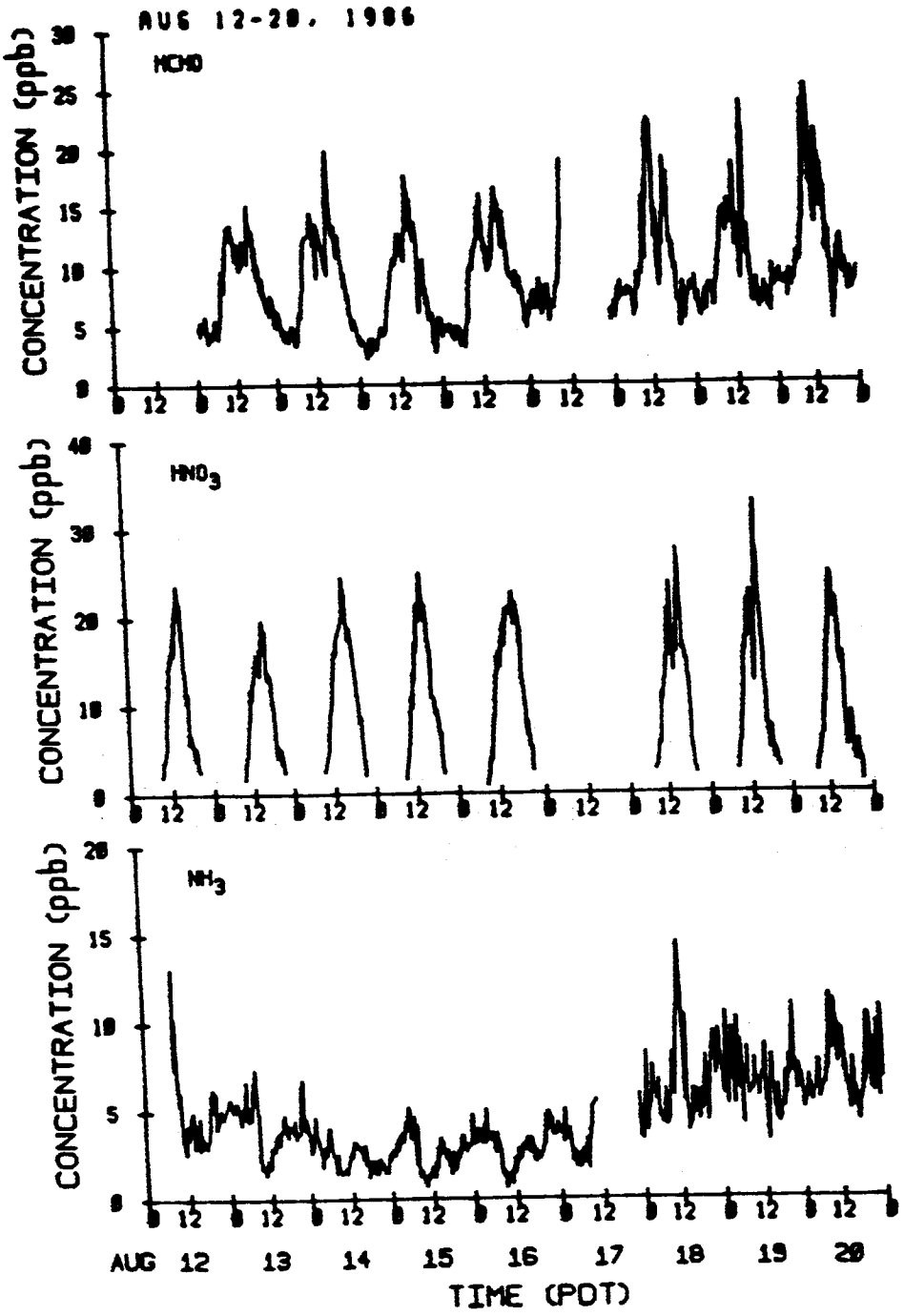


Figure V-6. Time-concentration profiles for formaldehyde, nitric acid and ammonia measured by long pathlength FT-IR spectroscopy during the 1986 Citrus College study.

Table V-2. Hourly Average HNO_3 Concentrations (ppb) at Glendora, CA, August 12-20, 1986, Measured by Long Pathlength FT-IR Spectroscopy

PDT	Aug 12	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20
0700-0800	<3	<3	<3	<3	<3	<3	<3	<3	<3
0800-0900	<3	<3	<3	<3	2.8	<3	3.3	5.5	3.6
0900-1000	3.4	3.0	x[a]	3.7	4.4	<3	5.9	10.8	5.9
1000-1100	7.1	6.7	x	8.3	9.0	x	11.0	17.0	10.2
1100-1200	13.1	10.5	x	12.3	14.2	x	14.0	20.1	16.5
1200-1300	15.9	13.3	14.8	17.1	15.8	x	19.6	18.7	22.5
1300-1400	18.2	15.0	x	20.7	18.0	x	17.1	22.6	21.2
1400-1500	22.0	15.6	x	22.7	20.3	x	17.2	23.9	19.0
1500-1600	19.6	18.1	22.3	20.3	20.9	x	23.9	15.6	14.9
1600-1700	11.9	14.9	19.3	14.3	20.4	x	19.2	7.8	8.9
1700-1800	6.1	12.4	17.4	9.9	19.5	x	14.9	6.5	6.2
1800-1900	4.9	8.0	13.3	7.9	12.6	x	8.9	4.8	7.2
1900-2000	3.3	4.9	9.5	4.0	7.8	x	3.4	3.7	4.7
2000-2100	<3	4.2	5.3	<3	4.5	x	<3	<3	4.6
2100-2200	<3	<3	<3	<3	<3	x	<3	<3	<3

[a] x - Designates no data due to power interruptions on August 14 and fault in archiving on August 17.

Table V-3. Hourly Average NH_3 Concentrations (ppb) at Glendora, CA, August 12-21, 1986, Measured by Long Pathlength FT-IR Spectroscopy[a]

PDT	Aug 12	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20	Aug 21
0000-0100		5.4	2.9	2.6	3.3	3.9	5.9	7.5	5.5	6.0
0100-0200		5.1	3.6	2.9	3.6	3.9	4.6	6.5	6.1	6.5
0200-0300		5.3	3.6	3.2	3.4	3.7	6.1	8.2	5.8	7.5
0300-0400		4.6	2.4	3.4	4.1	2.6	6.3	7.4	6.0	7.1
0400-0500		5.1	2.7	4.0	3.5	2.3	6.0	7.6	6.8	7.1
0500-0600		5.0	3.5	4.7	3.4	2.2	4.7	6.7	5.8	6.5
0600-0700		4.9	3.1	3.8	3.2	2.3	4.5	7.0	6.3	6.4
0700-0800		6.4	2.1	3.1	2.1	2.4	4.9	6.2	7.2	
0800-0900	8.8	5.1	1.9	1.8	1.3	3.8	5.7	6.6	9.9	
0900-1000	6.2	1.9	x[b]	1.1	1.1	5.4	7.1	6.7	10.0	
1000-1100	3.9	1.6	x	1.1	1.2	x	9.9	6.3	9.0	
1100-1200	3.4	1.9	x	1.4	1.9	x	13.2	7.3	8.9	
1200-1300	3.9	2.6	2.7	1.6	2.4	x	8.2	5.0	7.9	
1300-1400	4.4	3.1	x	2.3	2.6	x	6.4	6.2	6.3	
1400-1500	3.9	3.5	x	3.1	3.0	x	4.4	6.4	6.0	
1500-1600	3.7	3.8	2.6	2.6	2.9	x	5.8	5.2	6.2	
1600-1700	3.2	4.3	2.3	2.3	2.9	x	5.5	4.6	5.0	
1700-1800	3.1	3.8	1.7	2.1	2.4	x	5.4	5.4	5.5	
1800-1900	5.1	4.1	1.9	2.0	2.3	x	6.5	6.2	7.5	
1900-2000	5.9	4.0	1.8	2.3	2.9	x	5.6	7.4	9.7	
2000-2100	4.4	3.6	1.9	3.3	4.5	x	7.1	9.0	7.4	
2100-2200	4.8	5.3	2.0	3.1	4.1	x	8.5	6.9	7.1	
2200-2300	4.8	4.9	1.6	3.0	3.7	x	8.1	7.0	8.0	
2300-2400	5.2	4.1	2.2	3.7	3.9	3.9	7.5	6.3	8.4	

[a]Blank means outside the schedule.
[b]x - Designates no data due to power interruptions on August 14 and fault in archiving on August 17.

Table V-4. Hourly Average HCHO Concentrations (ppb) at Glendora, CA, August 13-21, 1986, Measured by Long Pathlength FT-IR Spectroscopy[a]

PDT	Aug 13	Aug 14	Aug 15	Aug 16	Aug 17	Aug 18	Aug 19	Aug 20	Aug 21
0000-0100	4.8	5.6	3.7	4.5	6.3	6.5	7.7	8.9	10.4
0100-0200	5.1	4.9	3.3	4.8	7.1	7.7	6.4	8.5	10.2
0200-0300	5.2	4.2	2.8	4.7	6.7	7.6	6.9	8.6	9.1
0300-0400	4.0	4.0	3.1	4.3	7.4	7.6	7.4	8.7	9.2
0400-0500	4.2	4.7	3.6	4.6	7.4	7.8	8.1	8.5	8.4
0500-0600	5.0	3.9	3.4	4.0	7.5	7.4	7.0	9.2	9.8
0600-0700	4.3	4.1	4.5	3.8	6.3	6.2	9.6	10.5	10.1
0700-0800	7.5	6.3	4.3	5.9	7.1	8.5	13.0	11.7	
0800-0900	9.2	10.1	6.5	9.7	9.4	9.7	14.5	19.5	
0900-1000	12.4	x[b]	9.0	11.2	15.4	13.8	14.2	22.5	
1000-1100	13.1	x	10.4	13.1	x	17.4	14.4	20.8	
1100-1200	11.9	x	11.7	14.5	x	21.1	14.4	15.9	
1200-1300	11.3	12.0	11.8	11.7	x	16.8	12.3	19.2	
1300-1400	10.6	x	11.7	10.1	x	10.5	14.5	17.1	
1400-1500	11.4	x	16.1	11.4	x	11.1	14.9	15.9	
1500-1600	11.9	15.9	15.1	14.8	x	15.7	10.6	12.2	
1600-1700	13.3	14.6	13.2	14.2	x	15.2	7.5	8.0	
1700-1800	12.1	12.7	9.0	13.2	x	11.6	8.1	7.6	
1800-1900	10.0	11.4	8.8	11.0	x	9.2	7.0	11.1	
1900-2000	8.4	9.9	8.0	9.1	x	6.4	7.3	10.5	
2000-2100	7.3	8.2	6.1	8.4	x	7.0	7.7	9.2	
2100-2200	6.4	6.3	4.8	8.5	x	6.2	6.9	8.6	
2200-2300	6.9	5.2	3.7	7.5	x	7.9	8.6	8.2	
2300-2400	6.0	4.2	5.1	5.4	6.1	8.2	8.6	9.0	

[a]Blank means outside the schedule.
[b]x - Designates no data due to power interruptions on August 14 and fault in archiving on August 17.

August 17 due to a fault in archiving the data onto magnetic tapes, the FT-IR system provided continuous coverage of HCHO and NH_3 concentrations since they were always above the respective detection limits of ~2-3 ppb and ~1-1.5 ppb. HNO_3 was generally above the ~3-4 ppb detection sensitivity between 0800 hr and 2000 hr each day throughout the study period. As for the 1985 Claremont and the 1986 Torrance studies, N_2O_5 was not observed above the estimated detection limit of 4 ppb.

The FT-IR analysis of formaldehyde was easily carried out with the use of single-beam spectra, since the HCHO infrared spectrum has a Q-branch at 2781.0 cm^{-1} well isolated from other atmospheric absorptions. HCHO was included as one of the species to be measured by FT-IR (except during the first day) because of the need for a standard against which other HCHO methods employed at this study could be compared. Our contribution to this aspect of the carbonaceous species study was to provide HCHO measurements by both DOAS and FT-IR spectroscopy, either method of which can serve as a benchmark standard. A comparison of the two sets of spectroscopic data for HCHO has been discussed in Section IV, and comparison with the results of the other HCHO methods is currently being carried out by Dr. Douglas Lawson of the CARB.

The NH_3 concentrations observed in Glendora (Table V-2) during the first six days of the field study (September 12-17) were generally in the range of 2-4 ppb. These levels are similar to those measured during the 1985 Claremont study for the periods when there was no localized transport of NH_3 to the latter site from nearby agricultural sources. NH_3 levels during the remaining days (August 18-21) were more variable and generally about twice the above range of values (Figure V-6). The erratic pattern found in the NH_3 concentrations during these three days, which is also noticeable in the more well-defined HCHO and HNO_3 concentration profiles (Figure V-6), could well be due to the prevailing wind conditions.

The maximum instantaneous concentrations of HNO_3 attained 20 ppb or higher during the eight days that the FT-IR measurements provided detailed HNO_3 profiles (Figure V-6), with the highest concentration of 33 ppb being observed on August 19. Comparison of our Dasibi ozone data with the FT-IR measurements of HNO_3 showed a strong correspondence between the HNO_3 and O_3 maxima. This is illustrated in Figure V-7 for the pollution episodes of August 15-16, where the hourly average HNO_3 concentrations (by FT-IR)

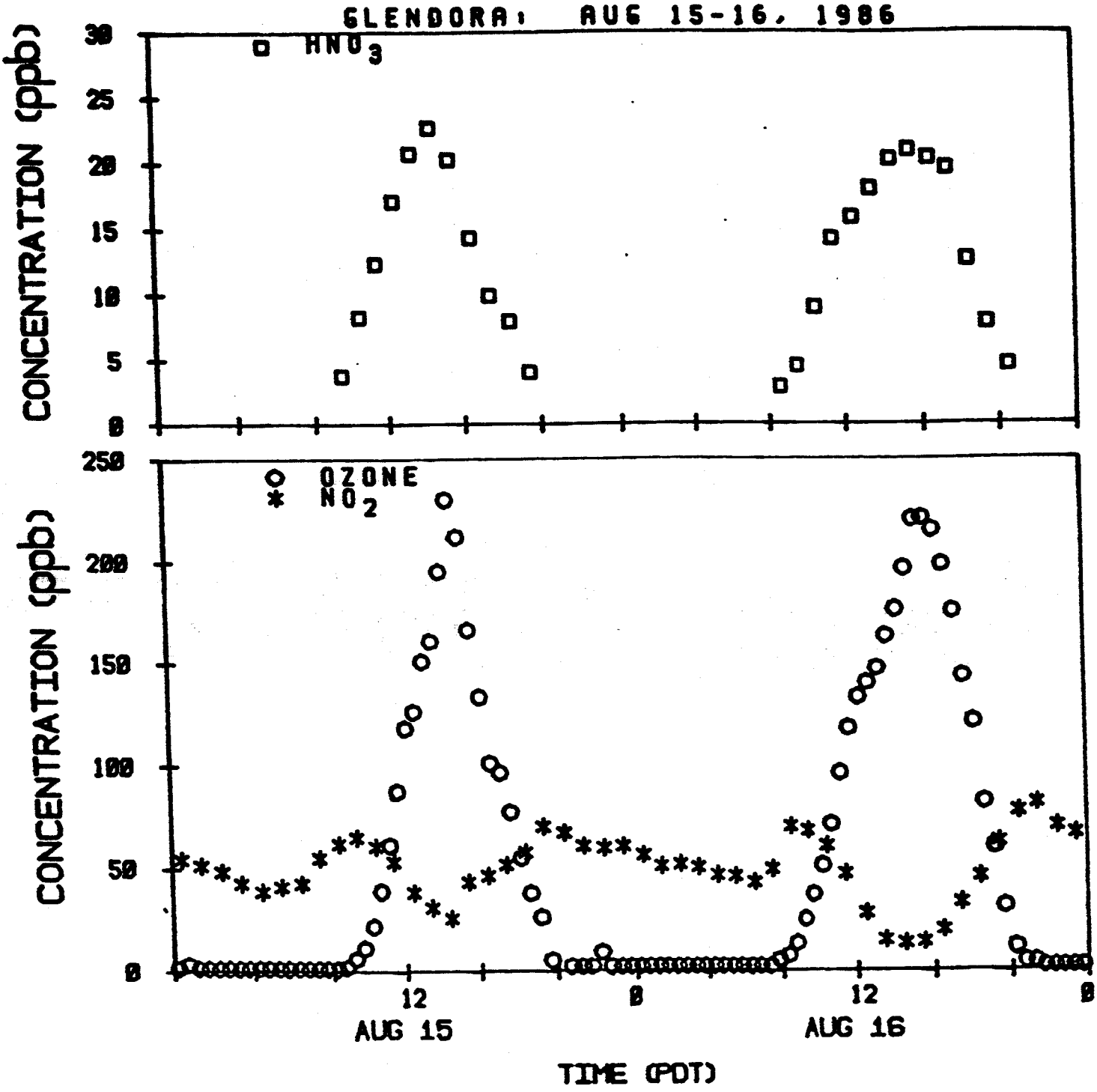


Figure V-7. Time-concentration plots of average HNO_3 (FT-IR), NO_2 (DOAS), and O_3 (Dasibi monitor) at Citrus College for August 15-16, 1986.

are compared with the half-hourly average O_3 concentrations. The correspondence of the HNO_3 concentration profile with that of the O_3 curve is even more pronounced in the similar plot in Figure V-8 for the August 18-19 episodes. Figures V-7 and V-8 also include the hourly average NO_2 concentrations (DOAS data, Section IV), which clearly show the expected minimum at the times of the maximum O_3 and HNO_3 concentrations. However, the maximum levels of HNO_3 observed in the afternoon could not be correlated with the maximum levels of NO_2 that prevailed during the morning hours.

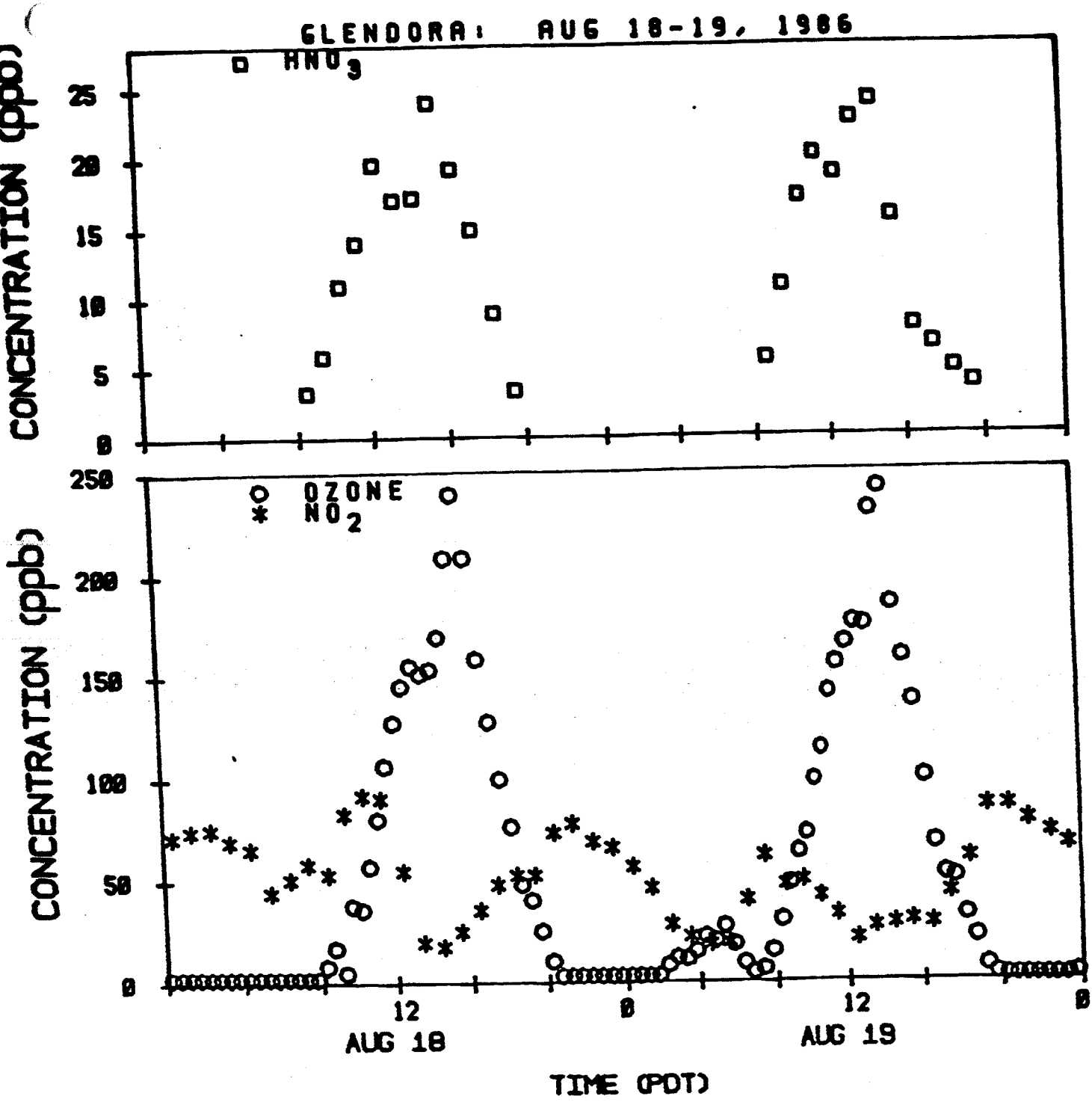


Figure V-8. Time-concentration plots of average HNO_3 (FT-IR), NO_2 (DOAS), and O_3 (Dasibi monitor) at Citrus College for August 18-19, 1986.

VI. AMBIENT CONCENTRATIONS OF PAH AND NITRO-PAH

A. Introduction

The PAH emitted from combustion sources exhibit a wide range of volatility, and are hence distributed in the atmosphere between the gas and particle phases. As we have shown previously (Arey et al. 1987), complementary sampling techniques are required to obtain a comprehensive data set concerning the concentrations of volatile and non-volatile PAH and their derivatives in the atmosphere. Thus, the volatile 2-ring PAH such as naphthalene, which are present almost entirely in the gas-phase, can be quantitatively collected on Tenax GC solid adsorbent. The non-volatile 5-ring and larger PAH and 3- to 4-ring nitro-PAH are particle associated and are collected totally on the Hi-vol filters. The 3- and 4-ring PAH of intermediate volatility and the 2-ring nitro-PAH can be collected on PUF plugs as well as on the filters, indicating that they are either present mainly in the gas-phase or are "blown-off" the filter during the collection period. Thus, three different collection media were employed for the ambient air sampling at Citrus College: Tenax-GC solid adsorbent, PUF plugs and Hi-vol filters. The ambient air samples were collected from August 12 to August 21, with 12-hr day (0800-2000 PDT) and night (2000-0800 PDT) sampling intervals.

B. Experimental

1. Sampling Media Cleaning Procedure

Tenax-GC solid adsorbent was Soxhlet extracted in a cellulose thimble for ~5 hr in a 6/4 (v/v) acetone/hexane mixture. After packing in Pyrex tubes (using precleaned glass wool) the Tenax cartridges were conditioned for ~4 hr by heating at 275°C with nitrogen flowing through them at ~20 mL min^{-1}. The Teflon-impregnated glass fiber (TIGF) filters and PUF plugs were cleaned by Soxhlet extraction for ~16 hr in methylene chloride, followed by another 16 hr extraction with methanol.

2. Tenax-GC Cartridges: Sampling and Analysis

Two sizes of Tenax-GC cartridge were used for the collection of gas-phase PAH at different flow rates. "Low-flow" cartridges consisted of 10 cm x 4 mm i.d. Pyrex tubes packed with 0.1 g of Tenax GC solid adsorbent, with sampling flow rates of ~1 L min^{-1}, yielding an ~0.6 m^3

volume of air for each 12-hr sampling period. "High-flow" cartridges consisted of 10 cm x 1 cm i.d. Pyrex tubes packed with 0.6 g of Tenax-GC and operated at flow rates of ~10 L min^{-1}, resulting in ~6 m^3 of air sampled during a 12-hr period. Each low-flow cartridge was equipped with back-up Tenax cartridge placed in series downstream from the first cartridge to check for breakthrough.

After sampling, the Tenax cartridges were stored in dry-ice, transported to SAPRC and stored in a freezer prior to analysis.

For analysis, deuterated internal standards were added to the low- and high-flow Tenax cartridges, respectively, as follows (in µg): naphthalene-d_8 (1.8, 16), biphenyl-d_{10} (0.7, 1.0), phenanthrene-d_{10} (0.6, 0.6). The low- and high-flow cartridges were eluted with 2 mL and 10 mL, respectively, of diethyl ether, which was then solvent exchanged to ~0.2 mL of acetonitrile (using a micro-Snyder apparatus for the high-flow cartridges).

PAH identifications and quantifications were made by combined gas chromatography/mass spectrometry (GC/MS) with multiple ion detection (MID), as described in detail below.

3. High-Volume Filters Followed by PUF Plugs: Sampling and Analysis

Two high-volume sampler systems consisting of a TIGF filter follow by four PUF plugs (~9 cm diameter x 5 cm thickness) [see Figure VI-1] were run at ~23 SCFM for 12 hr intervals, yielding ambient samples collected from ~1000 m^3 of air.

Prior to analysis, the PUF plugs were combined into six samples consisting of a single day sample and a single nighttime sample from the early portion of the study, single day and single night samples from the latter part of the study, and composite samples from four day and four nights. Specifically, the samples were: (#1) August 13, 0800-2000 hr; (#2) August 13-14, 2000-0800 hr; (#3) August 15, 16, 17, and 18, 0800-2000 hr; (#4) August 15-16, 16-17, 17-18, 18-19, 2000-0800 hr; (#5) August 20, 0800-2000 hr; (#6) August 20-21, 2000-0800 hr.

The samples from a single 12-hr day or night collection period (i.e., samples #1, 2, 5 and 6) each consisted of eight PUF plugs (four from each of the two Hi-vols used) and these were combined and extracted together. The composite samples #3 and #4 were each analyzed in two parts: PUF plugs #1-3 (see Figure VI-1) and, to check for breakthrough of the more

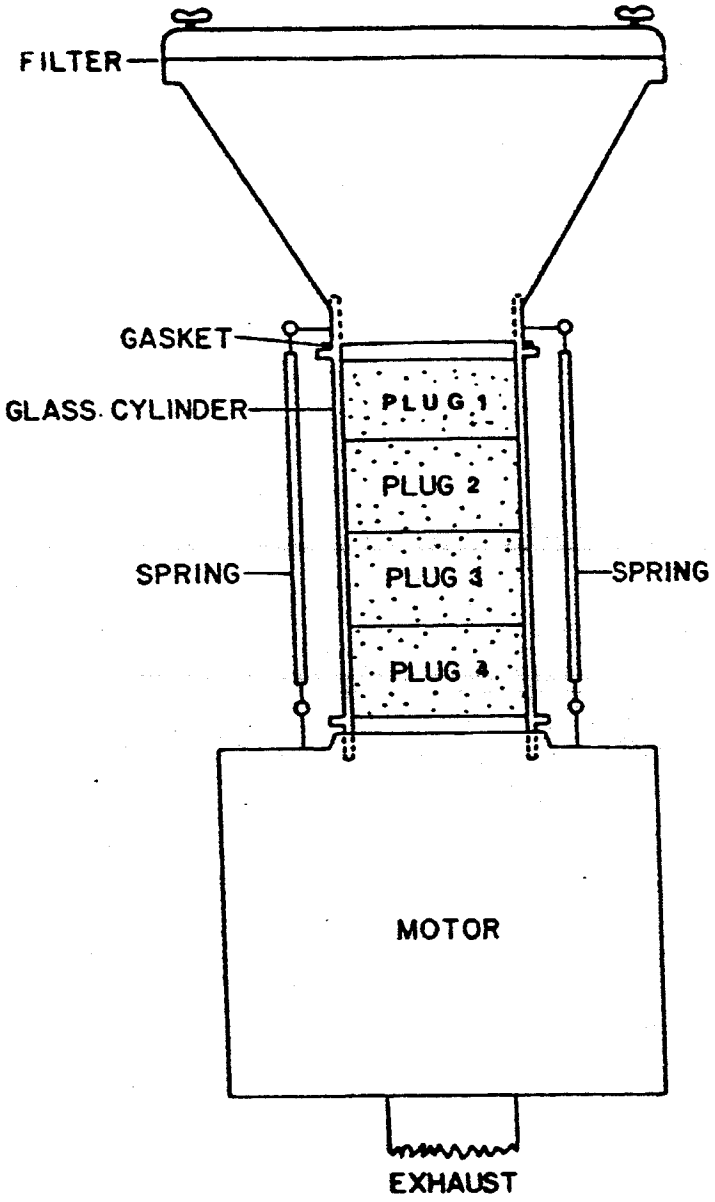


Figure VI-1. Schematic of modified Hi-vol sampler with PUF plugs underneath the filter to collect gas phase species and compounds "blown-off" the filter.

volatile PAH, PUF plugs #4. Prior to extraction, the PUF plugs were spiked with deuterated internal standards as follows (single 12-hr samples, composite samples, and fourth plugs, respectively, in μg): naphthalene-d_8 (3.27, 9.92, 2.48), biphenyl-d_{10} (3.27, 9.91, 2.48), phenanthrene-d_{10} (3.30, 10.01, 2.50), anthracene-d_{10} (3.69, 11.19, 2.48), benz(a)anthracene-d_{12} (1.34, 4.06, 1.02), chrysene-d_{12} (2.78, 8.43, 2.11), fluoranthene-d_{10} (3.51, 10.64, 2.66), pyrene-d_{10} (3.45, 10.46, 2.62), dibenzothiophene-d_8 (1.02, 3.08, 0.77), 1-nitronaphthalene-d_7 (0.35, 1.07, 0.27) and 2-nitrofluoranthene-d_9 (0.35, 1.07, 0.27). All samples were Soxhlet extracted overnight (~16 hr) with methylene chloride, concentrated by rotary evaporation under vacuum to ~4 mL, filtered through 0.45 μm Acrodiscs (Gelman Sci.) and concentrated further under a stream of nitrogen to ~500 μL.

The extracts were fractionated by HPLC using an Altex semi-preparative scale Ultrasphere Silica column (1 cm x 25 cm). Figure VI-2 shows a typical HPLC profile of a PUF plug extract together with the mobile phase program employed. A fraction containing the PAH was collected from 4 min to 22 min and a nitroarene-containing fraction from 22 min to 34 min. The fractions were concentrated by rotary evaporation, then taken just to dryness under a stream of nitrogen. After dissolving in acetonitrile or CH_2Cl_2, the PAH and nitroarene fractions were analyzed by GC/MS-MID as described below.

4. Hi-Vols with TIGF Filters: Sampling and Analysis

Seven Hi-vol samplers, each equipped with a 10 μm cut-off inlet, were employed for POM collection. The samplers were run at ~40 SCFM, yielding an ambient sample collected from ~800 m^3 of air for each Hi-vol over a 12-hr sampling period. Two Hi-vols were employed solely for the collection of POM used for mutagenicity testing. The TIGF filters from the remaining five Hi-vols were combined into six samples corresponding to the PUF plug samples described above, i.e., samples #1 and #2 and samples #5 and #6 comprised the single day and night samples from August 13-14 and August 20-21, respectively, and samples #3 and #4 were the composite day and night samples from August 15-16, 16-17, 17-18 and 18-19. The filter extraction and work-up procedure was as shown in Scheme VI-1. Each sample was spiked with deuterated internal standards as follows (single 12-hr samples and composite samples, respectively, in μg): fluoranthene-d_{10}

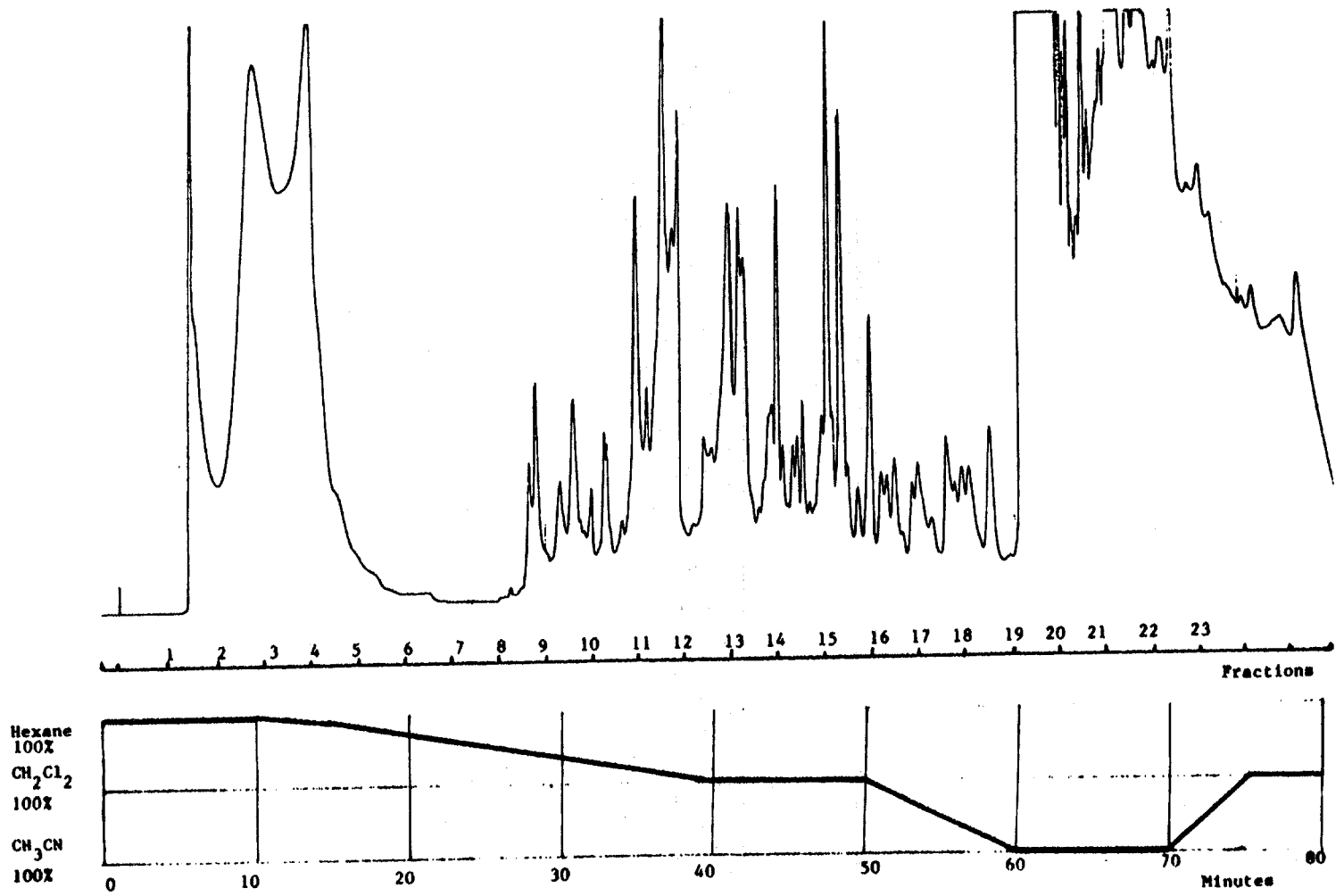
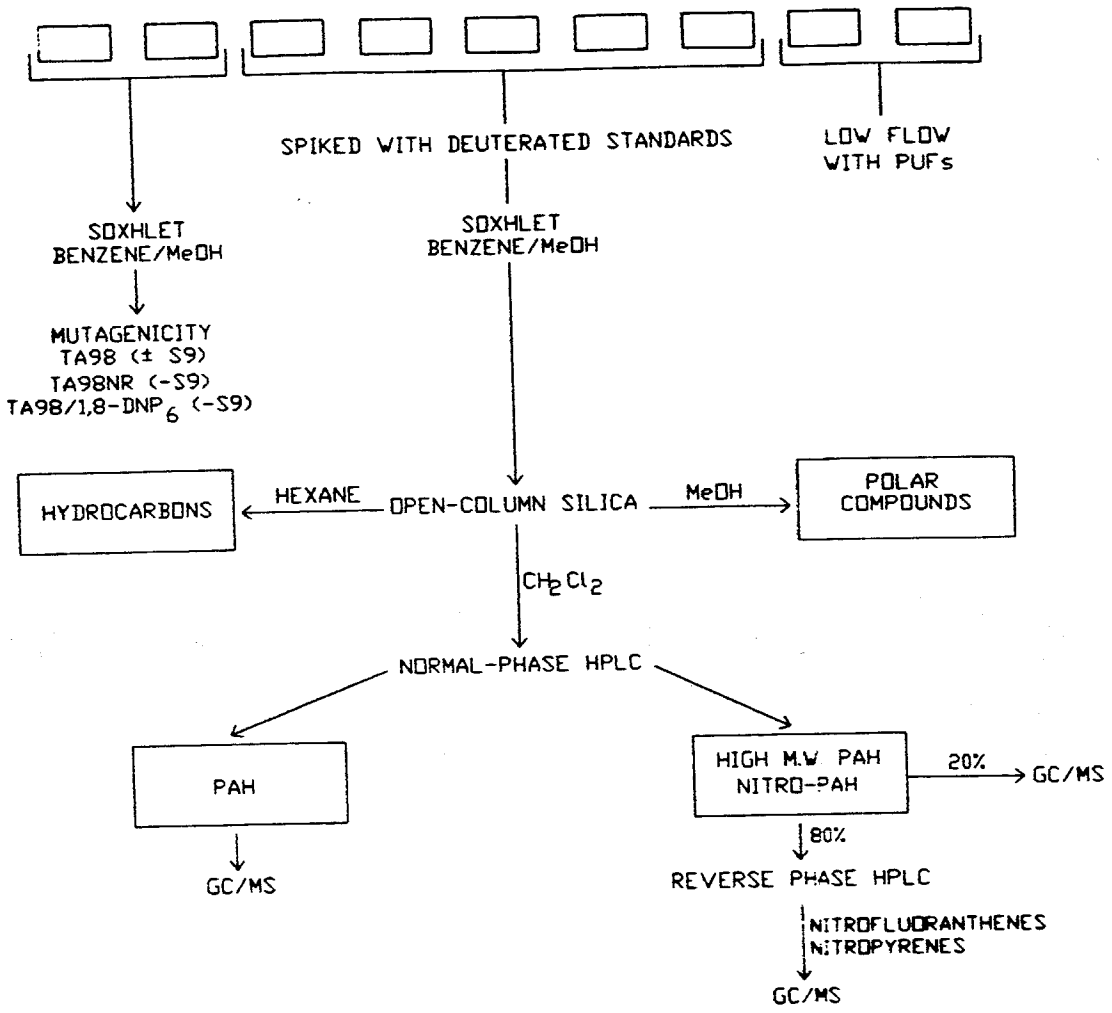


Figure VI-2. HPLC trace (254 nm) and gradient solvent program for separation of an ambient sample collected on PUF plug. Semi-preparative Ultrasphere Si column (1 cm x 25 cm), 3 mL min^{-1}. HPLC factions were combined as follows: #3-7, #8-11, #12, #13-15, #16-23.



Scheme VI-1. Outline of the chemical analysis procedure for a POM sample.

(10.6, 31.9), pyrene-d_{10} (10.4, 31.4), chrysene-d_{12} (5.27, 15.8), benz(a)-anthracene-d_{12} (2.13, 6.38), benzo(a)pyrene-d_{12} (2.81, 8.44), perylene-d_{12} (1.05, 3.14), dibenz(a,h)anthracene-d_{14} (1.98, 5.93), 1-nitronaphthalene-d_7 (0.54, 1.61), 2-nitrofluoranthene-d_9 (0.54, 1.61), 1-nitropyrene-d_9 (0.50, 1.51), dinitropyrene-d_8 mixture (1.98, 5.94). The filters were Soxhlet extracted overnight (16 hr) with benzene/methanol (4/1 v/v), and the extracts were concentrated by rotary evaporation and precleaned by open-column silica chromatography using sequential elution with hexane, CH_2Cl_2 and methanol (MeOH) to segregate the aliphatic hydrocarbons (eluted with hexane) and polar material (eluted with MeOH). The fraction of interest (eluted with CH_2Cl_2) was further fractionated by HPLC on a semi-preparative Altex Ultrasphere Silica column. Figure VI-3 shows a typical HPLC profile of the extract of an ambient POM sample together with the mobile phase program employed. The PAH-containing fraction was collected from 4 min to 13 min and a nitroarene-containing fraction from 13 to 25 min. The latter fraction contained the lower molecular weight nitroarenes as well as nitrofluoranthenes and nitropyrenes (mw 247) and some higher molecular weight PAH. This fraction was divided into two parts: 20% was analyzed by GC/MS-MID for PAH and lower molecular weight nitroarenes and 80% was fractionated further by reverse phase HPLC using an Altex semi-preparative Ultrasphere ODS column and isocratic elution with methanol/water (8/2 v/v). The fraction containing isomeric nitroarenes of mw 247 was then analyzed by GC/MS-MID (see below).

5. GC/MS Analyses

Compound identifications and quantifications were made using either a Finnigan 3200 quadrupole GC/MS interfaced to a Teknivent data system or a Hewlett Packard 5890 GC interfaced to a Hewlett Packard 5970 mass selective detector (MSD), both operated in the electron impact mode (70 eV). The GC separations were done either on a 60 m DB-5 fused silica capillary column with a cool on-column injection system (J & W Scientific, Inc.) or on a 30 m DB-5 fused silica capillary column with splitless injection. Both columns eluted directly into the MS ion source.

Calibration curves for the GC/MS-MID quantification of the PAH were made for the molecular ion peaks of the PAH using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as an internal standard. The

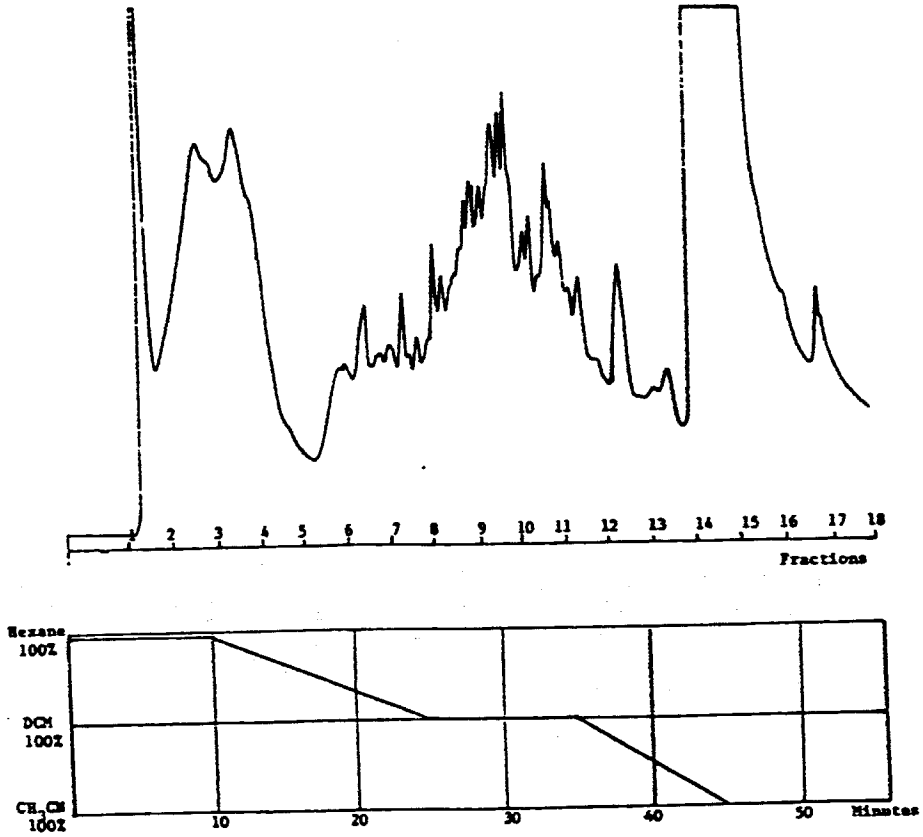


Figure VI-3. HPLC trace (254 nm) and gradient solvent program for separation of an ambient POM sample. Semi-preparative Ultrasphere Si column (1 cm x 25 cm), 3 mL min^{-1}. HPLC fractions were combined as follows: #2-5, #6-7, #8, #9, #10-13, #14-18.

National Bureau of Standards SRM 1647 (certified PAH) with the addition of biphenyl, methylnaphthalenes, dibenzothiophene and the deuterated internal standards was utilized to make the calibration solutions.

Identifications of the nitroarenes (apart from the methylnitronaphthalenes for which 14 isomers are possible) by GC/MS-MID were made on the basis of the presence, in correct abundance, of all of the major fragment ions as well as retention time matching. Authentic samples of all eight of the nitrofluoranthene and nitropyrene isomers and all three of the nitrobiphenyl isomers were available for retention time and fragment ion abundance comparisons. Quantifications for 1-nitronaphthalene, 2-nitrofluoranthene and 1-nitropyrene were made by comparison with deuterated internal standards. 2-Nitronaphthalene, 3-nitrobiphenyl and 9-nitroanthracene were quantified by external calibration of the molecular ion peak to that of the 1-nitronaphthalene-d_7 internal standard. 2-Nitropyrene and 3- and 8-nitrofluoranthene were quantified by external calibration using 1-nitropyrene-d_9 as the internal standard.

6. Chemicals

The following chemicals were obtained from commercial sources: phenanthrene-d_{10}, biphenyl-d_{10}, anthracene-d_{10}, pyrene-d_{10}, benzo(a)pyrene-d_{12} and perylene-d_{12} (Cambridge Isotope Laboratories); fluoranthene-d_{10} and dibenzothiophene-d_8 (MSD Isotopes Inc.); naphthalene-d_8, 1-nitronaphthalene-d_7, biphenyl, 1- and 2-nitronaphthalene, 2-, 3- and 4-nitrobiphenyl and 9-nitroanthracene (Aldrich Chemical Co.); 1- and 2-methylnaphthalene (Chem Services); Standard Reference Material 1647, certified PAH, (National Bureau of Standards). Commercially available 1-nitropyrene (Pfaltz and Bauer, Inc.) was purified according to the method described by Paputa-Peck et al. (1983).

2-Nitrofluoranthene-d_9 and 1-nitropyrene-d_9 were synthesized as described by Zielinska et al. (1986) and Pitts et al. (1985a). 2-Nitropyrene was provided by Dr. D. Schuetzle (Ford Motor Co.; Dearborn, MI) and 4-nitropyrene by Dr. A. Berg (University of Aarhus, Denmark). The 1-, 2-, 3-, 7- and 8-nitrofluoranthenes were synthesized as described previously (Ramdahl et al. 1985, Zielinska et al. 1986).

C. Results

1. Volatile PAH Sampled on Tenax-GC Cartridges

The most abundant PAH collected on the Tenax-GC cartridges were naphthalene and 1- and 2-methylnaphthalene. GC/MS analysis of Tenax samples in the full scanning mode (rather than the MID mode used for quantification) showed that, not unexpectedly, several alkylbenzenes were also very abundant. Table VI-1 summarizes the ambient concentrations (ng m^{-3}) of the volatile PAH measured. For reasons which will be detailed below, the naphthalene data from the low-flow cartridges have been utilized, while the data for the remaining PAH have been taken from the values obtained from the high-flow cartridges.

In Appendix B, Table B-1, the μg quantities of each PAH measured on the low-flow Tenax cartridges (for replicate GC/MS-MID quantifications) and the calculated total volumes for each sample are listed. Replicate injections gave reproducible values for naphthalene and 1- and 2-methylnaphthalene, while the levels of biphenyl, fluorene and phenanthrene were too low for accurate quantification. Also listed in Table B-1 are the quantities of PAH observed on the back-up Tenax cartridges, which were also generally too low for accurate quantification. Table B-2 lists the μg quantities measured and volumes sampled for the high-flow cartridges. Since the volumes of air sampled on the high-flow cartridges was a factor of 10 greater than the low-flow cartridges, biphenyl, fluorene and phenanthrene could be accurately determined, and in addition acenaphthylene and acenaphthene were measured.

Only traces of naphthalene were observed on the Tenax cartridges which were back-up cartridges for the low-flow Tenax, i.e., less than a few percent of that measured on the primary cartridge. Therefore, naphthalene was collected quantitatively on the low-flow Tenax. Table VI-2 compares the ambient naphthalene and 1- and 2-methylnaphthalene concentrations calculated from the low-flow and high-flow Tenax cartridges. The high-flow values for naphthalene were consistently lower than those obtained from the low-flow Tenax samples, indicating that naphthalene was not collected quantitatively at a collection rate of 10 L min^{-1} at the ambient temperatures encountered at Citrus College. Hence, the low-flow Tenax values for naphthalene are given in Table VI-1.

Table VI-1. Concentrations (ng m^{-3}) of Volatile PAH Sampled onto Tenax-GC Solid Adsorbent at Citrus College, Glendora, CA, in August, 1986 (Day, 0800-2000 PDT; Night, 2000-0800 PDT)

Date		ng m^{-3} [a]							
		Naphthalene[b]	1-Methylnaphthalene[c]	2-Methylnaphthalene[c]	Biphenyl[c]	Acenaphthylene[c]	Acenaphthene[c]	Fluorene[c]	Phenanthrene[c]
8/12/86	Day	2,200	150[d]	250[d]	-[e]	-[e]	-[e]	-[e]	-[e]
8/12-13/86	Night	5,000	500	900	220	39	32	49	64
8/13/86	Day	2,400	160	320	95	~3	4	30	26
8/13-14/86	Night	4,800	390	730	170	12	22	37	51
8/14/86	Day	2,500	130	260	70	~3	4	30	20
8/14-15/86	Night	3,000	330	640	100	23	17	34	40
8/15/86	Day	2,800	180[d]	190[d]	-[e]	-[e]	-[e]	-[e]	-[e]
8/15-16/86	Night	4,100	380	730	66	10	21	35	42
8/16/86	Day	3,200	98	200	52	~3	~4	23	16
8/16-17/86	Night	3,400	350	700	98	~3	24	40	37
8/17/86	Day	2,000	76	170	36	~3	~5	27	20
8/17-18/86	Night	4,300	330	680	54	4	30	47	51
8/18/86	Day	4,100	120	260	43	~3	5	31	26
8/18-19/86	Night	4,200	280	570	67	~3	28	43	46
8/19/86	Day	4,300	90	200	36	~3	4	23	21
8/19-20/86	Night	3,800	290	600	60	~3	28	44	50
8/20/86	Day	4,100	150	320	53	~3	6	33	29
8/20-21/86	Night	6,100	490[d]	860[d]	-[e]	-[e]	-[e]	-[e]	-[e]
AVERAGE DAYS		3,100	130	240	55	3	5	28	23
AVERAGE NIGHTS		4,300	370	710	100	12	25	44	48

[a] Average of replicate injections.
[b] Sampled at ~1 L min^{-1}.
[c] Sampled at ~10 L min^{-1}.
[d] Value from low-flow Tenax.
[e] High-flow Tenax sample lost.

Table VI-2. A Comparison of PAH Concentrations (ng m^{-3}) Measured on Low Flow and High Flow Tenax-GC Solid Adsorbent at Citrus College, Glendora, CA (Day, 0800-2000 PDT; Night, 2000-0800 PDT)

		ng m^{-3} [a]					
		Naphthalene		1-Methyl-naphthalene		2-Methyl-naphthalene	
Date		Low Flow[b]	High Flow[c]	Low Flow[d]	High Flow	Low Flow	High Flow
8/12/86	Day	2,200	-[e]	150	-[e]	250	-[e]
8/12-13/86	Night	5,000	2,200	460	500	860	900
8/13/86	Day	2,400	1,100	140	160	100	320
8/13-14/86	Night	4,800	1,900	430	390	720	730
8/14/86	Day	2,500	820	100	130	150	260
8/14-15/86	Night	3,000	1,600	340	330	680	640
8/15/86	Day	2,800	-[e]	180	-[e]	190	-[e]
8/15-16/86	Night	4,100	2,000	380	380	720	730
8/16/86	Day	3,200	690	130	98	60	200
8/16-17/86	Night	3,400	1,800	350	350	660	700
8/17/86	Day	2,000	470	60	76	50	170
8/17-18/86	Night	4,300	1,800	310	330	650	680
8/18/86	Day	4,100	670	110	120	120	260
8/18-19/86	Night	4,200	1,600	270	280	540	570
8/19/86	Day	4,300	500	100	90	110	200
8/19-20/86	Night	3,800	1,600	350	290	620	600
8/20/86	Day	4,100	810	180	150	180	320
8/20-21/86	Night	6,100	-[e]	490	-[e]	860	-[e]

[a] Average of replicate injections.
[b] Sampled at ~1 L min^{-1}.
[c] Sampled at ~10 L min^{-1}.
[d] Corrected by subtraction of average interference value as observed on back-up Tenax.
[e] High flow Tenax sample lost.

There is good agreement between the nighttime concentrations of the 1- and 2-methylnaphthalenes calculated from the low- and high-flow Tenax samples. For the daytime samples when the observed concentrations were generally low, the high-flow values tended to be somewhat higher than the low-flow values and were judged to be more accurate. It should be noted that the low-flow values for 1-methylnaphthalene have been corrected for a significant interference which was observed on the back-up Tenax.

2. PAH Sampled on PUF Plugs

GC/MS analysis of the HPLC fraction of the PUF plug extracts in which the PAH elute (see Figure VI-2) showed this fraction to contain many less abundant alkyl-PAH and dibenzothiophene as well as fluorene, phenanthrene, anthracene, fluoranthene and pyrene. It must be remembered that these PAH will be distributed between the gaseous and particle phases in ambient air and that the quantities measured on the PUF plugs are the sum of the PAH in the gas phase and the PAH initially present on the POM but "blown-off" during the collection period.

The ambient concentrations of five PAH and the sulfur heterocycle, dibenzothiophene, measured on the PUF plugs are given in Table VI-3. The most abundant PAH collected on the PUF plugs was fluorene. From the composite samples in which the fourth PUF plugs were analyzed separately, it was obvious that fluorene (mw 166) and PAH of higher volatility were not collected quantitatively on the PUF plugs since substantial amounts were present on the fourth PUF (see Table VI-3). Consistent with fluorene not being collected quantitatively on the PUF plugs, the ambient concentrations of fluorene listed in Table VI-1 from the Tenax cartridge quantifications are ~2-5 fold higher than those listed in Table VI-3. The ambient concentrations of phenanthrene measured on the PUF plugs and Tenax cartridges agree to within better than a factor of two.

Figure VI-4 shows the GC/MS-MID traces of naphthalene and alkylnaphthalenes for the Tenax and PUF samples from the evening of 8/13-14/86. From the Tenax sample trace it is clear that naphthalene was the most abundant species (at a measured concentration of ~5,000 ng m^{-3}). Comparing the Tenax and PUF sample traces it is apparent that naphthalene was retained on the PUF plugs only to a minor extent (with a measured concentration of ~2 ng m^{-3}). Interestingly, although not quantitatively collected on the PUF plugs, the presence of dimethylnaphthalenes in ambient air is apparent from the PUF samples.

Table VI-3. PAH Concentrations (ng m^{-3}) Measured on PUF Plugs at Citrus College, Glendora, CA

	Total Volume m^3	Fluorene[a]	Dibenzo-thiophene	Phen-anthrene	Anthra-cene	Fluor-anthene[b]	Pyrene[b]
Citrus College PUF Sample #1 8/13/86 0800-2000 PDT	469[c]	7.7	2.6	16.1	0.5	4.0	2.5
Citrus College PUF Sample #2 8/13-14/86 2000-0800 PDT	938	17.5	3.3	23.2	1.9	6.2	5.5
Citrus College PUF Sample #3 Day Composite 0800-2000 PDT 8/15,16,17,18/86	3,751	5.4	2.3	14.4	0.3	4.2	2.4
4th PUF Day Composite	3,751	4.4	0.3[d]	1.5	0.04	0.03	0.02
Citrus College PUF Sample #4 Night Composite 2000-0800 PDT 8/15-16,16-17,17-18,18-19/86	3,751	14.1	3.0	22.2	1.2	5.2	4.0
4th PUF Night Composite	3,751	11.6	0.05[d]	0.2	ND[e]	0.02	0.03
Citrus College PUF Sample #5 8/20/86 0800-2000 PDT	938	6.2	2.7	19.0	0.5	5.9	3.6
Citrus College PUF Sample #6 8/20-21/86 2000-0800 PDT	938	20.8	4.5	31.8	1.8	6.8	4.9

[a]Not quantitative, a lower limit due to breakthrough.
[b]Some present on the particles as well.
[c]Only a single Hi-vol sample utilized; second Hi-vol not operating correctly.
[d]Based on a single injection.
[e]ND = None detected.

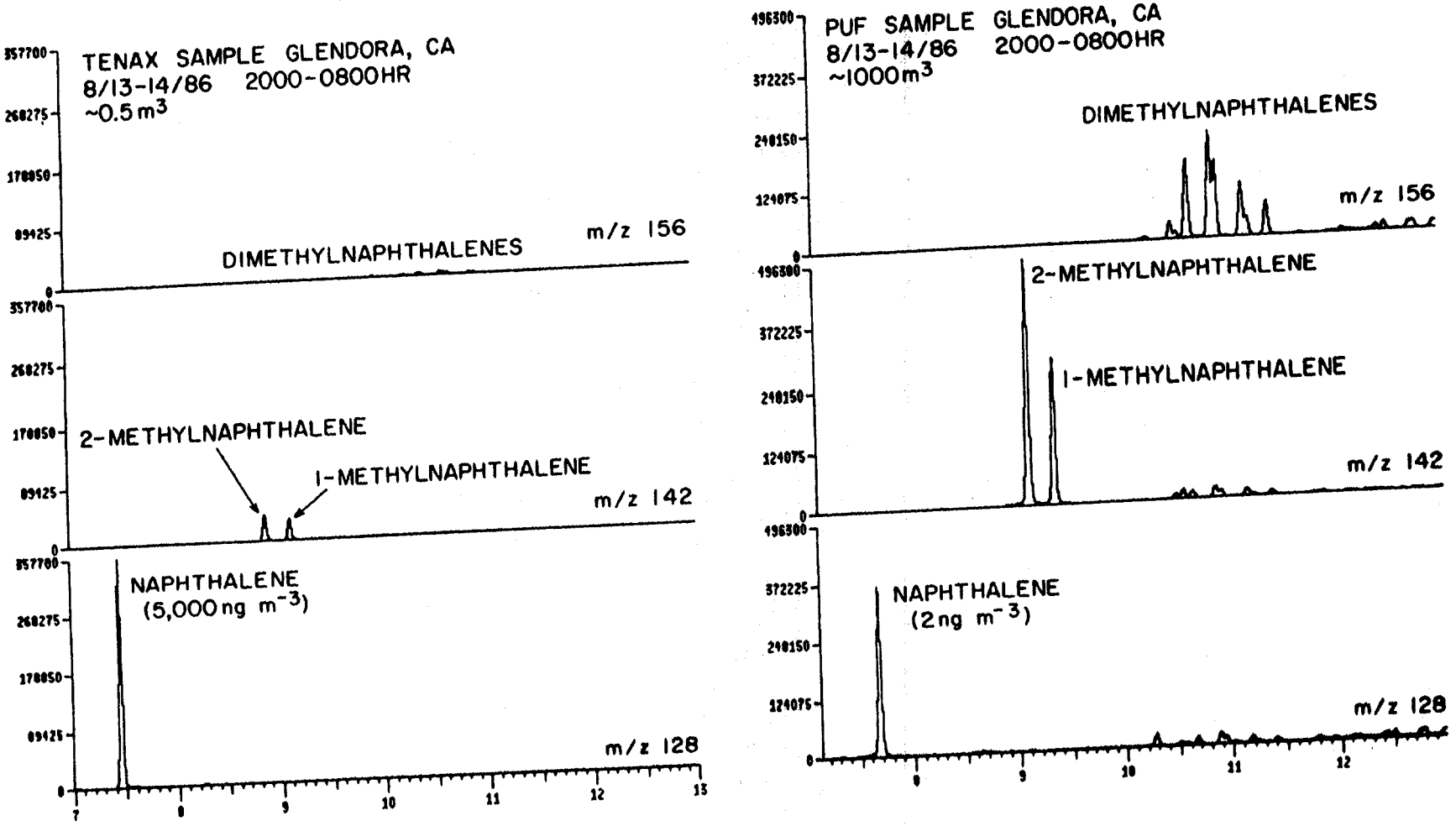


Figure VI-4. GC/MS-MID traces showing the molecular ions of naphthalene (m/z 128), 1- and 2-methylnaphthalene (m/z 142) and the dimethylnaphthalenes (m/z 156) for analyses of a Tenax-GC (left) and PUF plug (right) sample collected simultaneously in Glendora, CA, on 8/13-14/86 from 2000-0800 PDT. The abundances of naphthalene and the alkylnaphthalenes collected on the PUF plug sample are similar and do not reflect the true ambient concentrations. Note the quantitative naphthalene concentration of ~5,000 ng m^{-3} measured by the Tenax sample vs. 2 ng m^{-3} as measured by the PUF sample.

3. Diurnal Variations in the Volatile PAH

The ambient concentrations of naphthalene measured for 12-hr day and night sampling intervals throughout the Citrus College study are shown in Figure VI-5. It can be seen from these data that the naphthalene concentrations were generally higher during the evening sampling intervals and that there was a trend toward higher concentrations in the latter part of the study.

The daytime and nighttime concentrations of 1- and 2-methylnaphthalene are shown in Figure VI-6. As observed for naphthalene, the nighttime concentrations were generally higher. The concentration of 2-methylnaphthalene was consistently higher than that of 1-methylnaphthalene. The concentration profiles of the methylnaphthalenes were remarkably similar, perhaps indicating a common source and similar atmospheric loss processes. Reaction with the hydroxyl radical is expected to be the major loss process for both species, with essentially identical atmospheric lifetimes for 1- and 2-methylnaphthalene (Atkinson and Aschmann 1987a).

All of the volatile PAH were generally more abundant during the nighttime than daytime sampling intervals (see Table VI-1 and VI-3). Meteorological factors such as inversion heights may certainly have played a role in this observed trend at Citrus College, but it can be seen that these diurnal variations are not solely due to meteorology by comparing the diurnal profiles of species of differing reactivity. For example, the GC/MS-MID traces for the molecular ion of biphenyl and acenaphthene (m/z 154) for a typical daytime and nighttime Tenax sample are shown in Figure VI-7. As seen from this figure, acenaphthene [the more reactive of these PAH (Atkinson and Aschmann 1987b)], was generally significantly more abundant in the nighttime samples, presumably being removed by rapid reaction with the OH radical during daylight hours.

GC/MS-MID traces of daytime and nighttime PUF samples showing the analyses of isomeric PAH of differing reactivity are shown in Figures VI-8 and VI-9. While phenanthrene was abundant on both the day and nighttime PUF plug samples, the relative abundance of anthracene to phenanthrene was consistently higher at night (Figure VI-8). Similarly, acephenanthrylene, an isomer of fluoranthene and pyrene expected to be more reactive than these PAH towards ozone (Atkinson and Aschmann 1987b), was generally not observed in the daytime PUF samples from Citrus College (Figure VI-9).

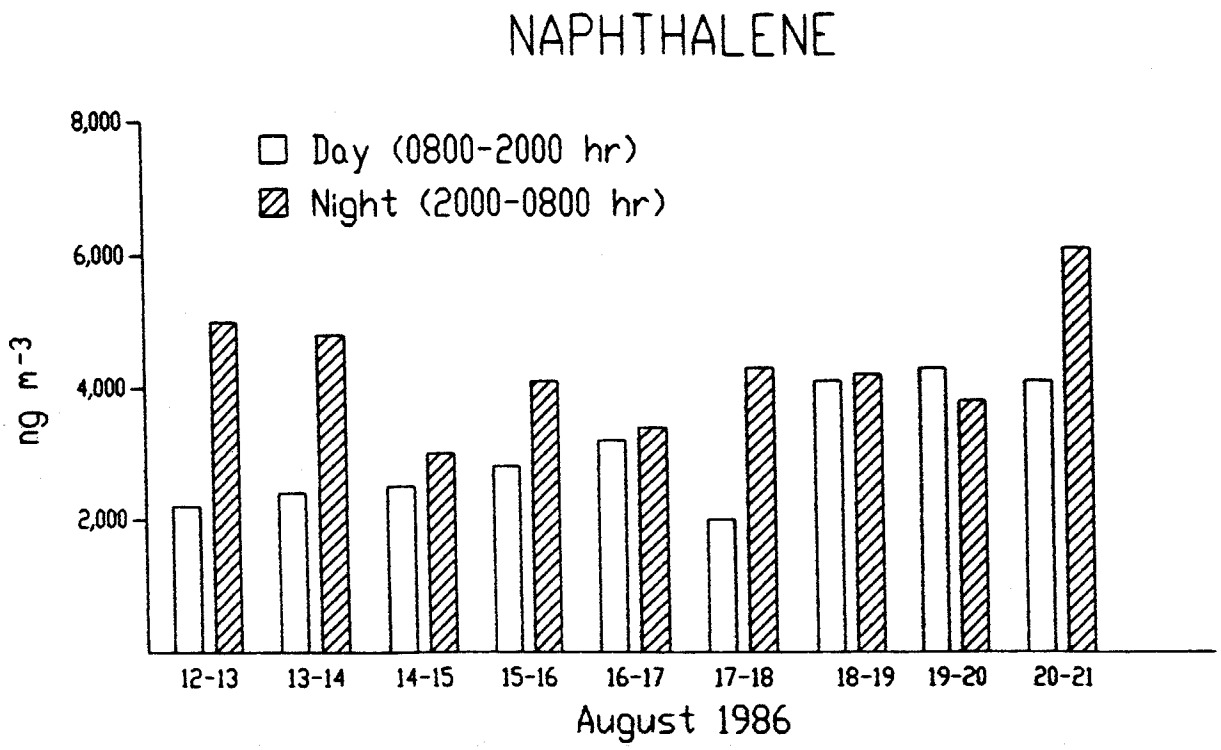


Figure VI-5. Diurnal variations in naphthalene concentration at Citrus College in Glendora, CA.

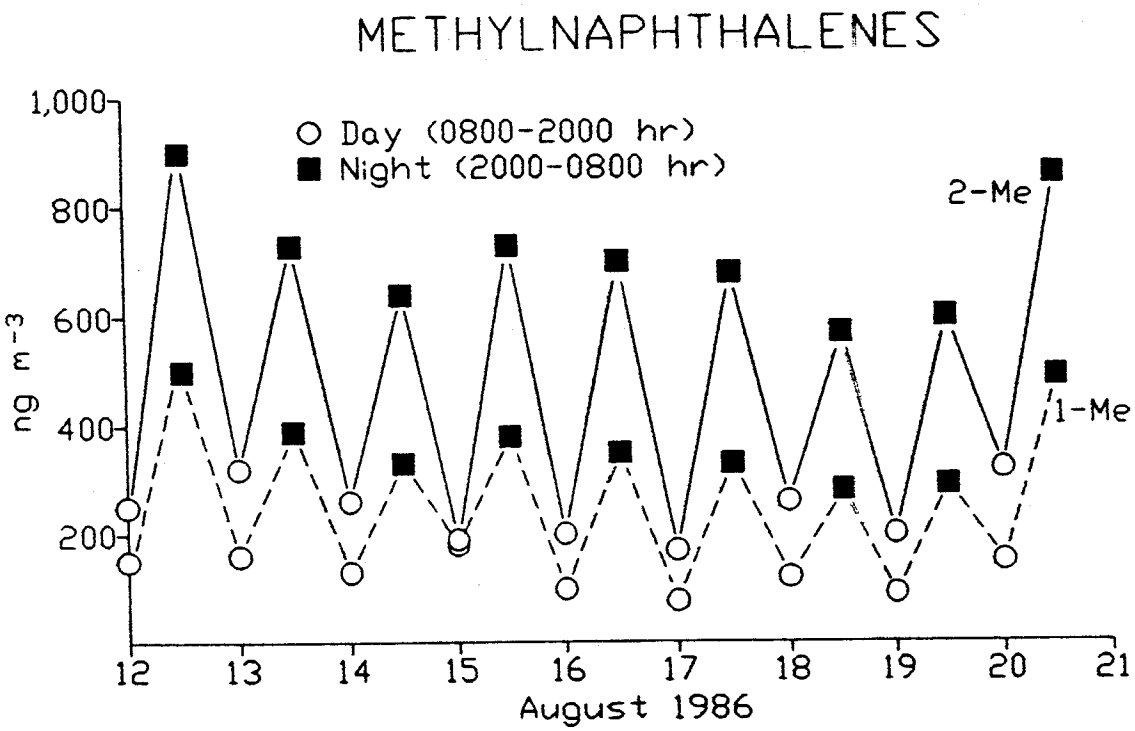


Figure VI-6. Diurnal variation in the concentrations of 1-methylnaphthalene (1-Me) and 2-methylnaphthalene (2-Me) at Citrus College in Glendora, CA.

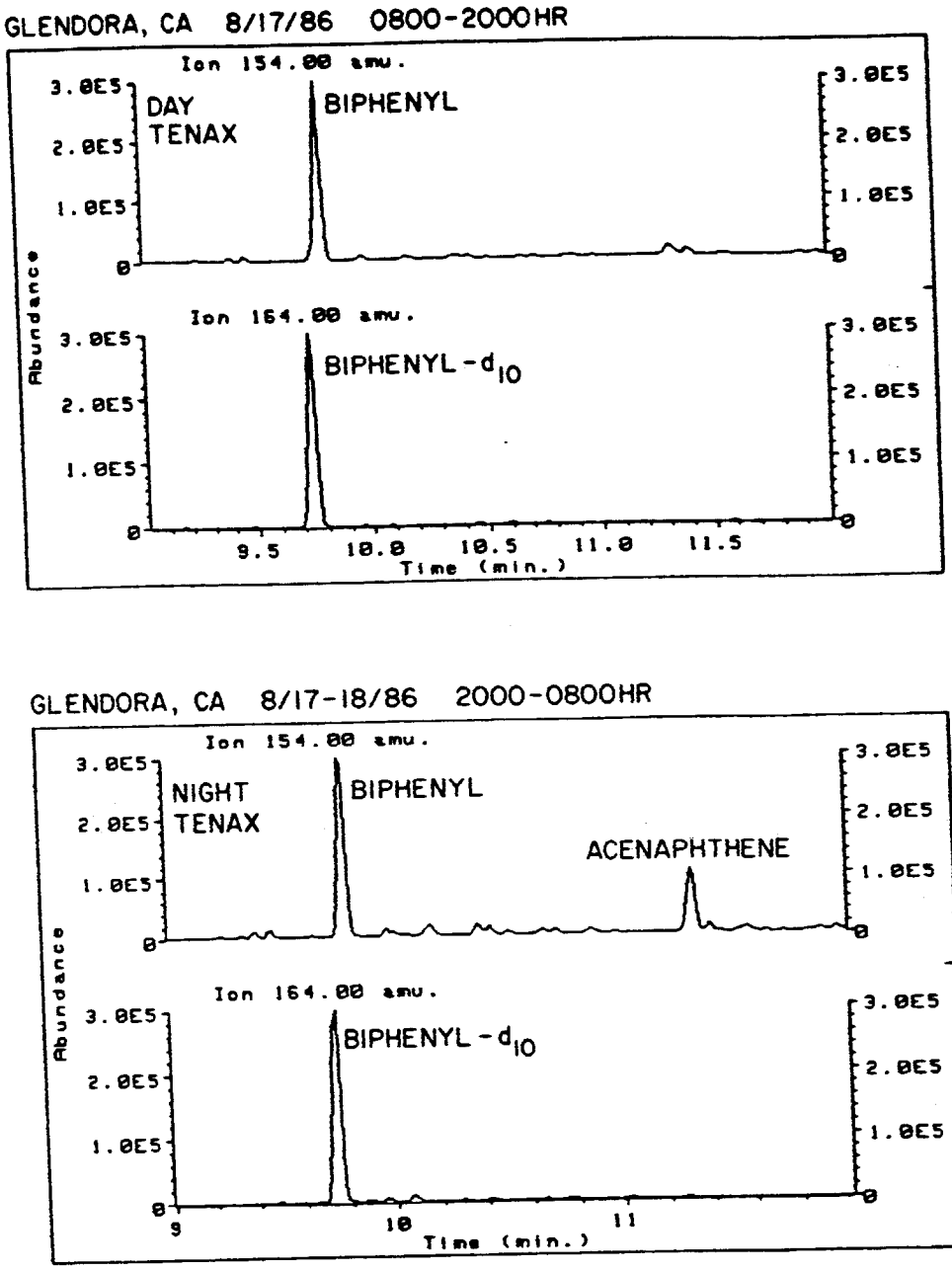


Figure VI-7. GC/MS-MID traces for the molecular ion of biphenyl and acenaphthene (m/z 154) and the deuterated internal standard, biphenyl-d_{10} (m/z 164) from the analyses of a daytime (top) and nighttime (bottom) ambient air sample collected on Tenax-GC solid adsorbent at Citrus College, Glendora, CA.

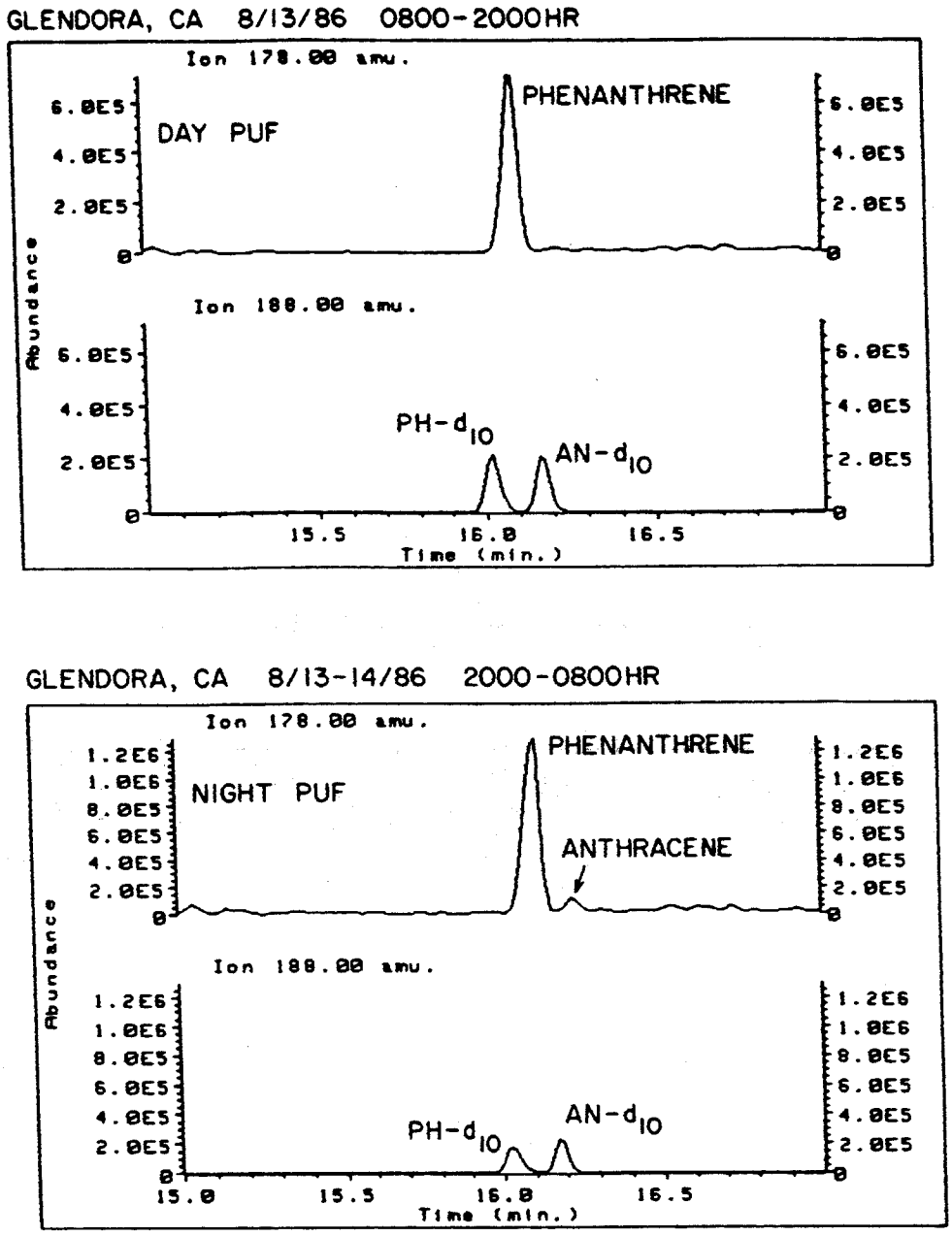


Figure VI-8. GC/MS-MID traces for the molecular ion of phenanthrene (PH) and anthracene (AN) [m/z 178] and their corresponding deuterated species (m/z 188) utilized as internal standards from the analyses of a daytime (top) and nighttime (bottom) ambient air sample collected on PUF plugs at Citrus College, Glendora, CA.

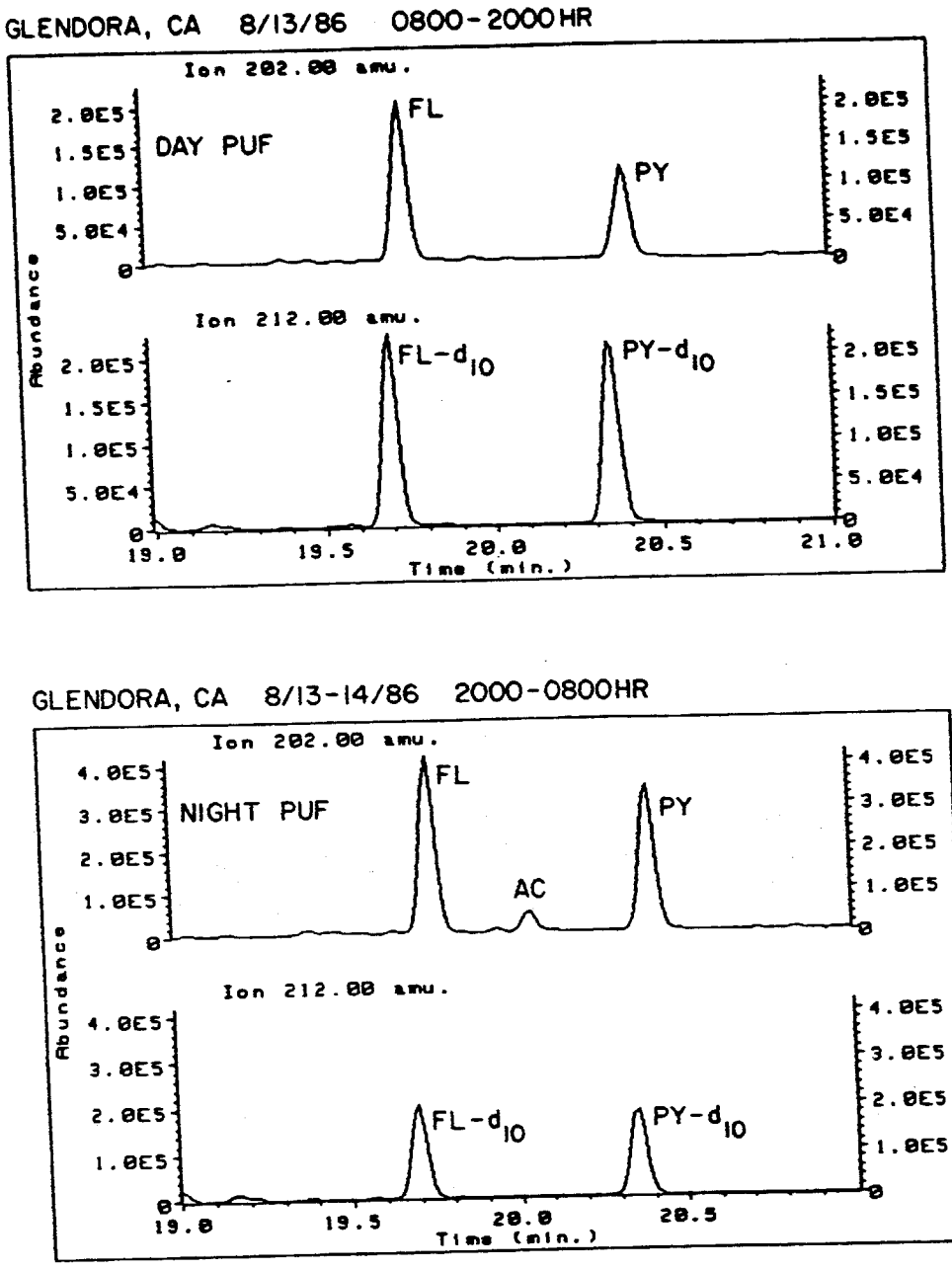


Figure VI-9. GC/MS-MID traces for the molecular ion of fluoranthene (FL), pyrene (PY) and acephenanthrylene (AC) [m/z 202] and the deuterated internal standards FL-d_{10} and PY-d_{10} (m/z 212) from the analyses of a daytime (top) and nighttime (bottom) ambient air sample collected on PUF plugs at Citrus College, Glendora, CA.

4. Nitroarenes Sampled on PUF Plugs

The HPLC fraction of the PUF plug extracts eluting from 22 to 34 min (Figure VI-2) contained the volatile nitroarene species. The most abundant nitroarenes were 1- and 2-nitronaphthalene. GC/MS analysis in the full scanning mode showed that this nitroarene-containing HPLC fraction also contained alkylnitrophenols.

Figure VI-10 shows GC/MS-MID traces from a typical analysis of a Citrus College PUF plug extract for 1- and 2-nitronaphthalene (NN). As seen from this figure, identification was based on the presence of several characteristic fragment ions, as well as retention time matching with the 1-nitronaphthalene-d_7 internal standard. Figure VI-11 shows the presence of several peaks at m/z 187 which elute after 1- and 2-nitronaphthalene. These peaks were identified as methylnitronaphthalenes (14 isomers are possible) on the basis of the presence of characteristic $[M-NO_2]^+$ and $[M-HNO_2]^+$ fragment ions as well as the m/z 187 molecular ion.

GC/MS-MID traces of a standard mixture of the three nitrobiphenyl isomers and two isomers of nitroacenaphthene are shown in Figure VI-12. 5-Nitroacenaphthene has previously been reported in ambient air (Tokiwa et al. 1981). At Torrance, CA, during a wintertime high-NO_x episode, we did not observe nitroacenaphthene, but measured high concentrations of the isomeric species, 3-nitrobiphenyl (Arey et al. 1987). In Figure VI-13 the $[M]^+$ ions of the standard mixture are shown together with the $[M]^+$ ions and characteristic fragment ion traces obtained from the analysis of a Citrus College PUF plug sample. As at Torrance, CA, the nitroarene isomer of mw 199 observed at Citrus College was clearly 3-nitrobiphenyl.

Table VI-4 gives the μg quantities of 1- and 2-nitronaphthalene and 3-nitrobiphenyl collected on the PUF plugs at Citrus College. From the fourth PUF plugs of the composite samples, it can be seen that 3-nitrobiphenyl was quantitatively collected on the first three PUF plugs. Particularly during the daytime samples, some breakthrough of 1- and 2-nitronaphthalene occurred. In addition to these nitroarene species, traces of 9-nitroanthracene were observed in most of the Citrus College PUF plug samples, but the levels present were too low to quantify.

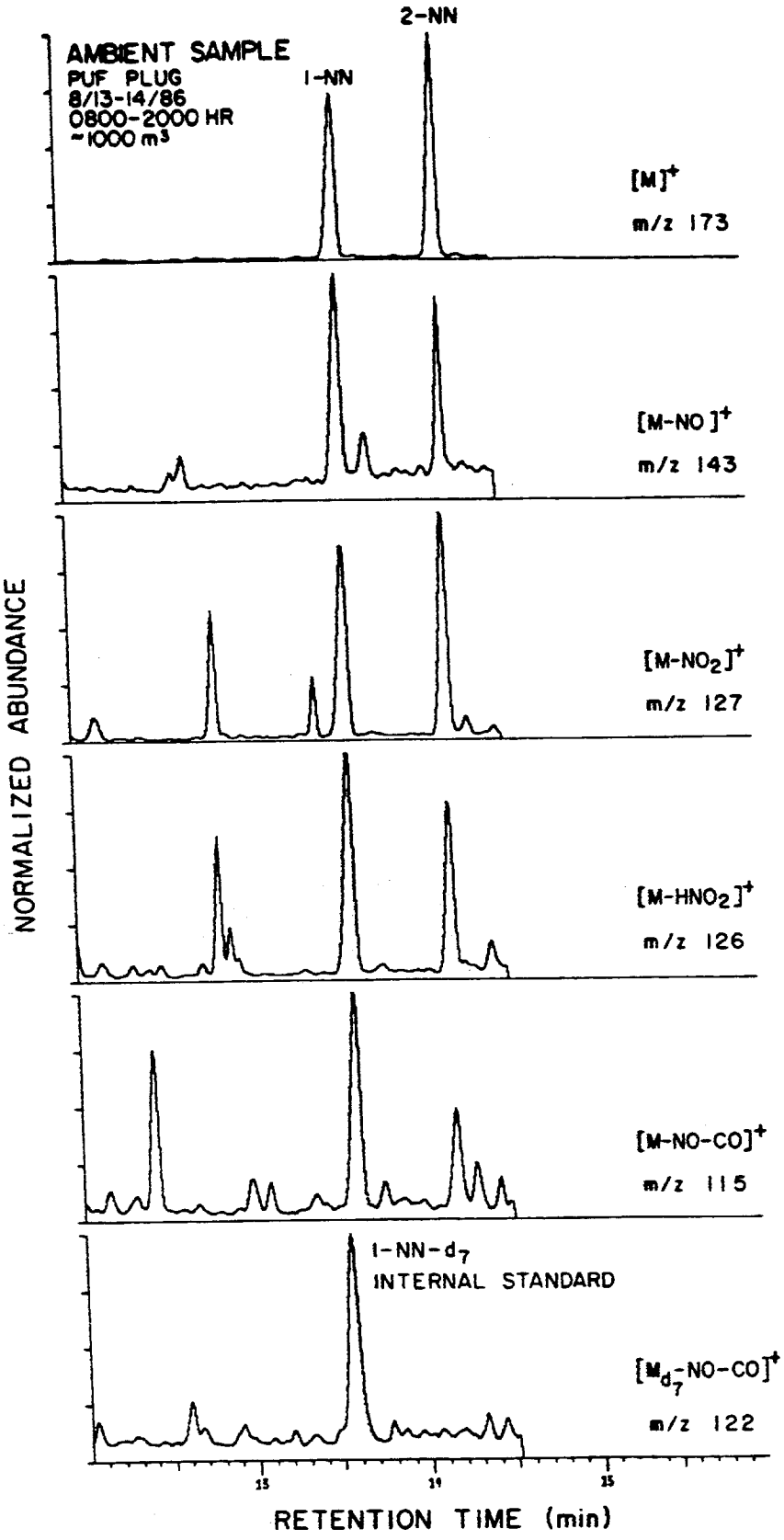


Figure VI-10. GC/MS-MID traces for the molecular ion (m/z 173) and several characteristic fragment ions of 1- and 2-nitronaphthalene (NN) and an abundant fragment ion from the deuterated internal standard 1-NN-d_7 showing the presence of 1-NN and 2-NN in an ambient air sample collected on PUF plugs at Citrus College, Glendora, CA.

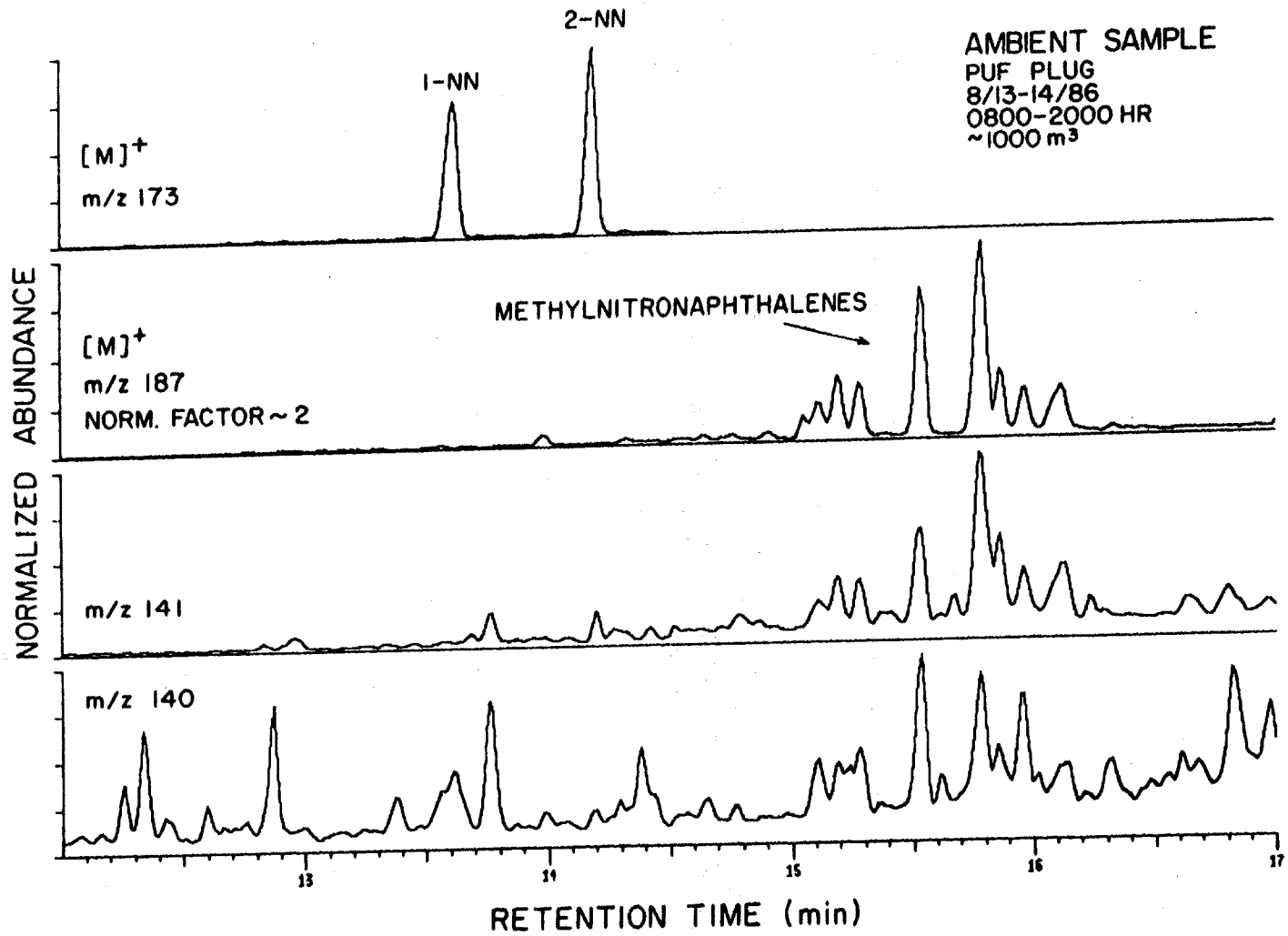


Figure VI-11. GC/MS-MID traces showing the presence of methylnitronaphthalenes in an ambient air sample collected on PUF plugs at Citrus College, Glendora, CA.

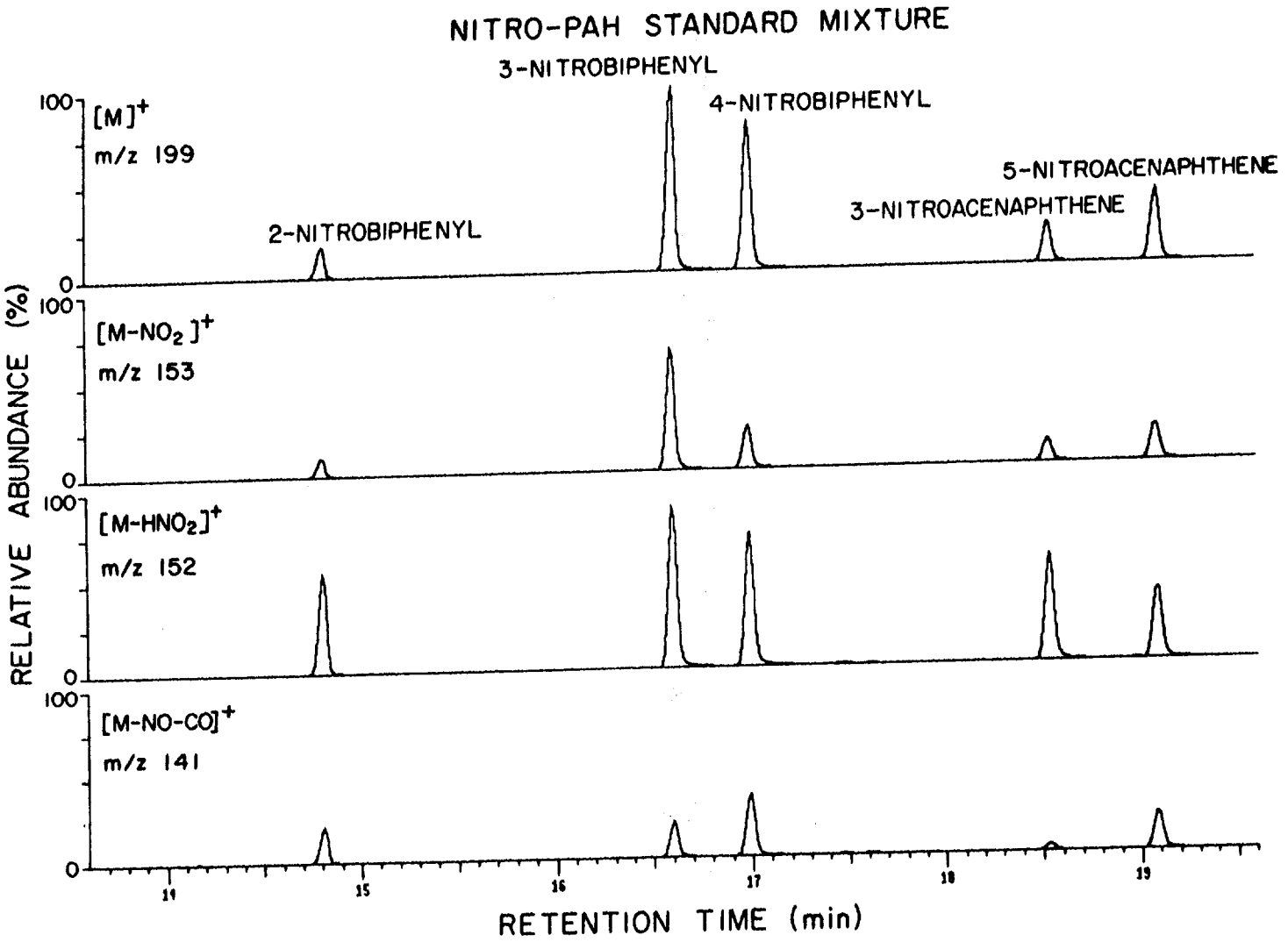


Figure VI-12. GC/MS-MID traces from the analysis of a standard mixture of the isomeric nitrobiphenyls and nitroacenaphthenes showing their excellent resolution on the 30-m DB-5 capillary column utilized.

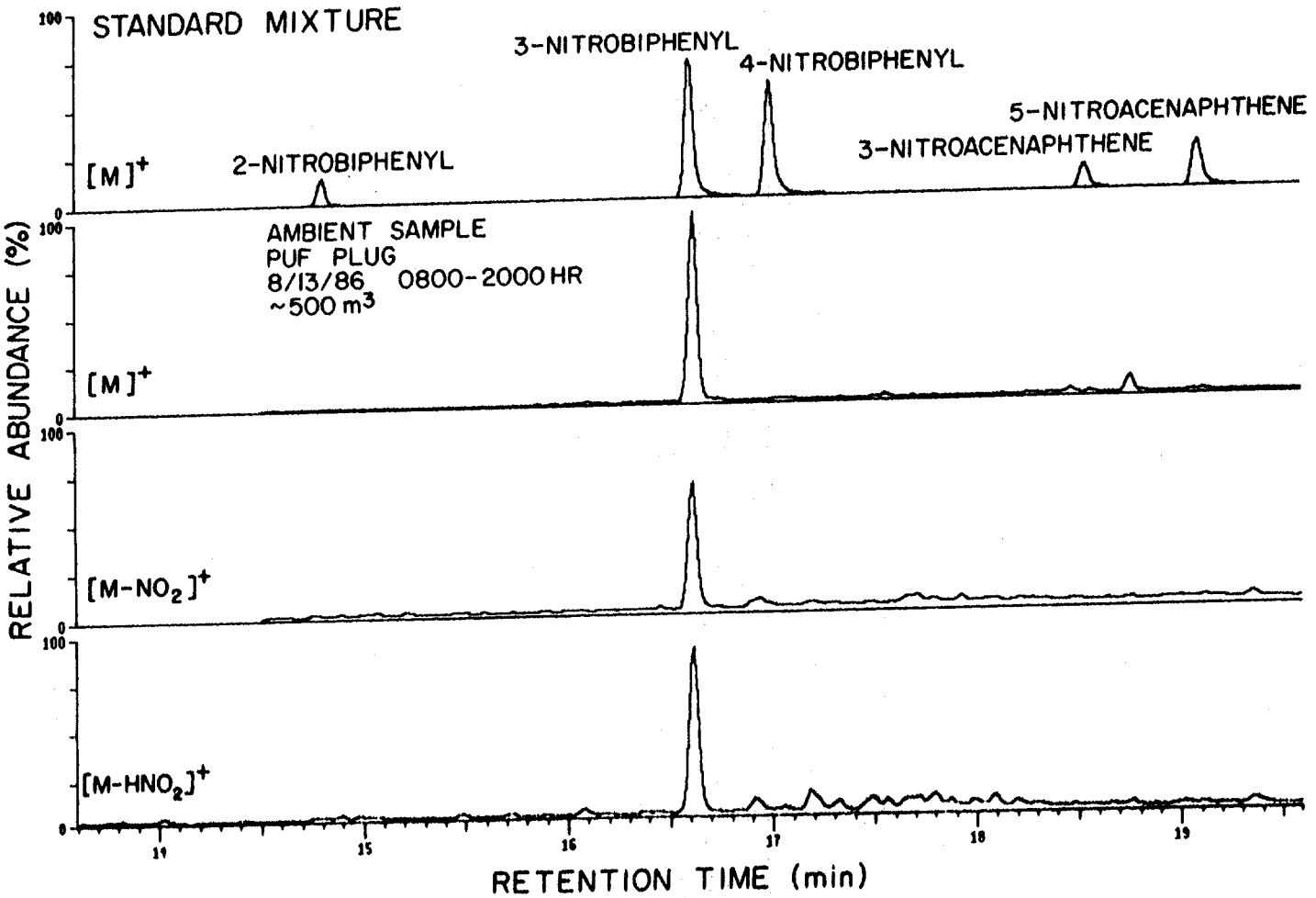


Figure VI-13. GC/MS-MID traces showing 3-nitrobiphenyl to be present in an ambient air sample collected on PUF plugs at Citrus College, Glendora, CA. The top trace repeats the molecular ion trace of the standard mixture (Figure VI-12) and it can be seen that the peak in the ambient sample (the molecular ion and two characteristic fragment ions shown) exactly matches 3-nitrobiphenyl in retention time.

Table VI-4. Nitro-PAH Measured on PUF Plugs at Citrus College, Glendora, CA

	Total Volume[a] m^3	Replicate GC/MS-MID Quantifications (µg) 1-Nitronaph-thalene	2-Nitronaph-thalene	3-Nitro-biphenyl
Citrus College PUF Sample #1 8/13/86 0800-2000 PDT	469[b]	1.06 1.12	0.85 0.83	0.56 0.60
Citrus College PUF Sample #2 8/13-14/86 2000-0800 PDT	938	2.30 2.59	1.49 1.57	0.39 0.45
Citrus College PUF Sample #3 Day Composite 0800-2000 PDT 8/15,16,17,18/86	3,751	7.48 8.04	8.09 8.43	2.92 3.35
Sample #3 4th PUF Day Composite		1.47 1.27	0.73 1.04	0.08 ND[c]
Citrus College PUF Sample #4 Night Composite 2000-0800 PDT 8/15-16,16-17,17-18,18-19/86	3,751	11.65 11.86	7.51 7.31	1.19 1.28
Sample # 4 4th PUF Night Composite		0.52 0.57	0.09 0.22	0.01 ND
Citrus College PUF Sample #5 8/20/86 0800-2000 PDT	938	2.44 2.59	2.41 2.45	0.79 0.87
Citrus College PUF Sample #6 8/20-21/86 2000-0800 PDT	938	5.16 5.56	2.64 3.26	0.41 0.45

[a]Run at 23 SCFM.
[b]Only a single Hi-vol sample utilized.
[c]ND = None detected.

Table VI-5 summarizes the ambient concentrations of 1- and 2-nitronaphthalene and 3-nitrobiphenyl. As observed at Torrance, CA, the daytime concentrations of 3-nitrobiphenyl were consistently higher than the nighttime concentrations, reflecting the daytime atmospheric formation of this species (Arey et al. 1987). At Torrance, both 1- and 2-nitronaphthalene

were observed to be lower in the nighttime sample than the daytime sample (Arey et al. 1987) again reflecting their daytime formation by hydroxyl radical-initiated reaction (Atkinson et al. 1987). In contrast, at Citrus College 1-nitronaphthalene was consistently higher in the nighttime than in the daytime samples. The likely operation of a second atmospheric formation mechanism for the nitronaphthalenes, by reaction of naphthalene with N_2O_5 during early evening hours, will be discussed in Section VIII.

Table VI-5. Nitroarene Concentrations Measured on PUF Plugs[a] at Citrus College, Glendora, CA

Sample Site and Date	pg m^{-3}		
	1-Nitro-naphthalene	2-Nitro-naphthalene	3-Nitro-biphenyl
PUF Sample #1 8/13/86 0800-2000 PDT	2,320	1,790	1,240
PUF Sample #2 8/13-14/86 2000-0800 PDT	2,610	1,630	450
PUF Sample #3 8/15,16,17,18/86 Day Composite 0800-2000 PDT	2,430	2,440	840
PUF Sample #4 8/15-16, 16-17,17-18,18-19/86 Night Composite 2000-0800 PDT	3,280	2,020	330
PUF Sample #5 8/20/86 0800-2000 PDT	2,680	2,590	880
PUF Sample #6 8/20-21/86 2000-0800 PDT	5,710	3,140	460

[a] Σ 4 PUF plugs.

5. PAH Sampled on TIGF Filters

As described in Section B above, the extracts of the TIGF filters were fractionated by HPLC. HPLC fractions #2-5 (see Figure VI-3) were collected as the PAH fraction, with fractions #6-7 being chosen to include the nitroarenes. Through the use of deuterated internal standards, it became apparent that the higher molecular weight PAH such as dibenz(a,h)-anthracene were eluting in HPLC fractions #6-7. The data reported here for the PAH on filters will be for the lower molecular weight species, i.e. fluoranthene, pyrene, benz(a)anthracene, chrysene/triphenylene and benzo(a)pyrene. Fractions #6-7 will be analyzed for the higher molecular weight PAH and the full range of data for PAH on particles will be given in our final report for our on-going CARB project (Contract No. A5-185-32), "A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California."

Table VI-6 lists values for fluoranthane, pyrene, benz(a)anthracene, chrysene/triphenylene and benzo(a)pyrene in the NBS SRM 1649, an air particulate sample collected in Washington, D.C. The values recently reported by the NBS (Wise et al. 1986) for analyses by GC and HPLC with fluorescence detection along with our values determined by GC/MS-MID are given. The extraction and clean-up procedures we used for the SRM particles were as described in Section B for the Citrus College POM sample analyses. As can be seen from Table VI-6, the agreement between our values and those reported by NBS is generally excellent.

The μg quantities of the five PAH measured in the Citrus College POM samples for replicate GC/MS-MID quantifications are given in Appendix B, Table B-3. The concentrations of these five PAH in ng m^{-3} (averaging the replicate values) are given in Table VI-7. Two additional samples, #7 and #8, repeat day and night composites, are also listed in Tables B-3 and VI-7. It was found that in taking the benzene/methanol extracts to a constant weight a significant fraction of the deuterated internal standards fluoranthene-d_{10}, pyrene-d_{10} and even 2-nitrofluoranthene-d_9 were lost. The use of internal standards should, of course, allow for correction of such losses. Since all of the filters from each day or night comprising these composites had not been extracted, we made replicate composite samples and extracted these replicates with dichloromethane. As can be seen from Table VI-7, the composites and the repeat composites

agree to within better than a factor of two. In our current procedure for POM analyses, the benzene/methanol extract is not taken to dryness.

6. Nitroarenes Sampled on TIGF Filters

The ambient concentrations of the nitrofluoranthenes and nitropyrenes measured for the six Citrus College POM samples are given in Table VI-7. As we have observed previously (Pitts et al. 1985c, Ramdahl et al. 1986, Arey et al. 1987), 2-nitrofluoranthene was the most abundant particle-associated nitroarene. The GC/MS-MID trace of the molecular ion for the nitrofluoranthenes and nitropyrenes (m/z 247) from the August 20-21, 1986, 2000-0800 PDT sample is shown in Figure VI-14. This sample represents the highest ambient concentration of 2-nitrofluoranthene that we have observed to date, being 2 ng m^{-3} of 2-nitrofluoranthene.

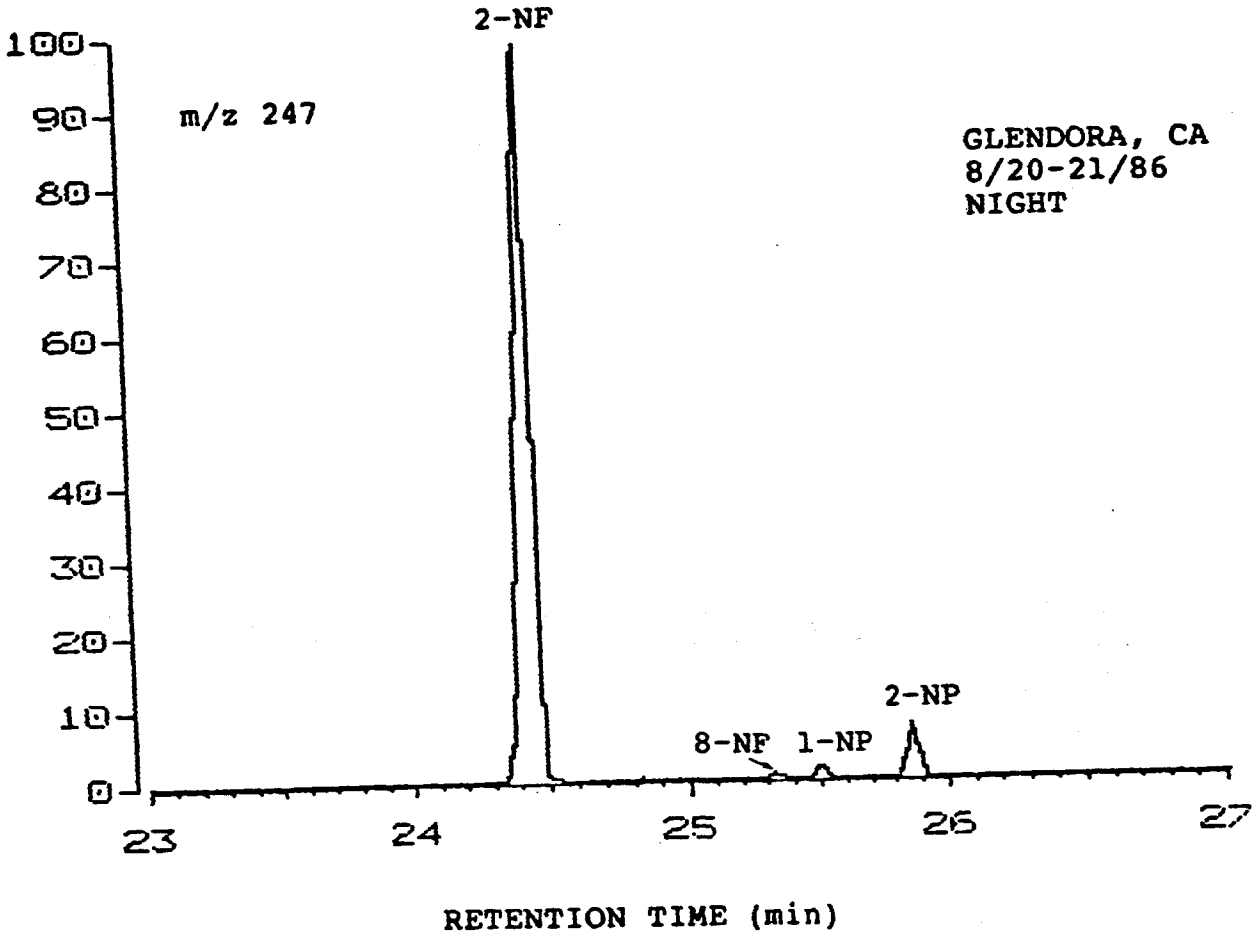


Figure VI-14. GC/MS-MID trace showing the molecular ion of the nitrofluoranthenes (NF) and nitropyrenes (NP) analyzed in an ambient POM sample collected at Citrus College, Glendora, August 20-21, 1986, from 2000-0800 PDT.

Table VI-6. PAH in NBS Standard Reference Material 1649, Washington, D.C., Air Particulate Sample

PAH	μg g^{-1} NBS Values[a] GC	NBS Values[a] LC	SAPRC Values for Replicate GC/MS Analysis
Fluoranthene	7.3 ± 0.2	7.1 ± 0.5	7.1, 7.0
Pyrene	7.2 ± 0.2	6.0 ± 0.2	6.2, 6.1
Benz(a)anthracene	2.4 ± 0.1	2.4 ± 0.1	2.3, 2.1
Chrysene/ triphenylene	4.6 ± 0.2	3.5 ± 0.1 1.7 ± 0.1	4.0, 3.9
Benzo(a)pyrene	3.0 ± 0.3	2.4 ± 0.2	2.3, 2.2

[a]Wise et al. (1986).

Table VI-7. PAH Concentrations Measured on Particles Collected on TIGF Filters at Citrus College, Glendora, CA

Sample Site and Date	ng m^{-3}				
	Fluor-anthene	Pyrene	Benz(a)-anthracene	Chrysene/ Triphenylene	Benzo(a)-pyrene
Filter Sample #1 8/13/86 0800-2000 PDT	0.23	0.46	0.15	0.50	0.21
Filter Sample #2 8/13-14/86 2000-0800 PDT	0.24	0.32	0.20	0.73	0.48
Filter Sample #3 Day Composite 0800-2000 PDT 8/15,16,17,18/86	0.22	0.21	0.10	0.30	0.12
Filter Sample #4 Night Composite 2000-0800 PDT 8/15-16,16-17,17-18,18-19/86	0.16[a]	0.26[a]	0.06	0.27	0.15
Filter Sample #5 8/20/86 0800-2000 PDT	0.29	0.32	0.11	0.43	0.17
Filter Sample #6 8/20-12/86 2000-0800 PDT	0.20	0.22	0.12	0.37	0.18
Filter Sample #7[b] Repeat Day Composite 8/15,16,17,18/86	0.30	0.32	0.13	0.55	0.17
Filter Sample #8[b] Repeat Night Composite 3/15-16,16-17,17-18,18-19/86	0.24	0.28	0.17	0.62	0.27

[a]Single injection.
[b]Extracted in CH_2Cl_2.

Table VI-8. Concentration (pg m^{-3}) of Nitrofluoranthenes and Nitropyrenes in Ambient POM at Citrus College, Glendora, CA

Sample	2-Nitro-fluoranthene	3-Nitro-fluoranthene	8-Nitro-fluoranthene	1-Nitro-pyrene	2-Nitro-pyrene
Filter Sample #1 8/13/86 0800-2000 PDT	200	ND[a]	3	20	17
Filter Sample #2 8/13-14/86 2000-0800 PDT	480	ND	7	31	50
Filter Sample #3 Day Composite[b] 8/15,16,17,18/86	220	15	3	8	7
Filter Sample #4 Night Composite[b] 8/15-16,16-17,17-18,18-19/86	950	18	4	10	21
Filter Sample #5 8/20/86 0800-2000 PDT	410	Traces	2.5	12	13
Filter Sample #6 8/20-21/86 2000-0800 PDT	2,000	Traces	4	14	42

[a]ND = None detected.
[b]Extracted with CH_2Cl_2.

VII. AMBIENT MUTAGENICITY

A. Introduction

For the past several years, the mutagenicity of ambient POM has been recognized as a characteristic of polluted urban atmospheres. Furthermore, although airborne particulate matter contains many carcinogenic PAH, its mutagenic activity does not resemble that of the PAH, which require mammalian metabolic activation (S9) as a requisite for expression of their mutagenicity in the Ames Salmonella test. Instead, ambient POM is "directly active," i.e., expressing mutagenicity without the addition of S9, and thus showing that other classes of organic chemicals, which are direct-acting mutagens, are also present in ambient air.

As an integral part of the CSMCS carried out at Citrus College, Glendora, we measured the mutagenicity of collected 12-hour particulate samples, both with and without mammalian metabolic activation, on Salmonella strain TA98. Additionally, we obtained mutagenicity data on strains TA98NR and TA98/1,8-DNP_6.

B. Experimental

Sample Preparation for Mutagenicity Testing. As noted in Section III, POM samples were collected on a 12-hr basis throughout the study period, from 0800-2000 and 2000-0800 PDT. The collected particulate matter from two Hi-vols fitted with 10 μm cut-off inlets was weighed, and the filters Soxhlet extracted for 16-hr using a benzene/methanol (80/20) azeotrope. The solvent was removed under vacuum and the extracts were taken to dryness under a stream of dry nitrogen. Prior to mutagenicity testing, the sample extracts were stored in the dark at -75°C. On the day of the test, each extract was taken up in DMSO using a 20-minute sonication, and serial dilutions in DMSO were made from this stock solution.

Tester Strains. Ames Salmonella strain TA98 was used because of its sensitivity to atmospheric particulate mutagens such as the nitroarenes (Rosenkranz and Mermelstein 1983), and each particulate extract was tested on this strain both in the presence and the absence of mammalian metabolic activation (S9). Each sample was also tested on strains TA98NR and TA98/1,8-DNP_6 in the absence of S9 as a possible indication of nitroarene

mutagenicity. TA98NR and TA98/1,8-DNP_6 are isolates of TA98 which are deficient in a nitroreductase (Rosenkranz and Speck 1975, McCoy et al. 1981) and a transacetylase enzyme (McCoy et al. 1983, Orr et al. 1985, Saito et al. 1985), respectively. The deficiency of these enzymes, which are required in the activation of many nitroarenes to penultimate mutagens, renders these strains less sensitive than TA98 to many mutagenic nitroarenes. Thus, when a complex mixture exhibits less activity on TA98NR or TA98/1,8-DNP_6, relative to TA98, it may be an indication of the contribution of nitroarenes to the mutagenic activity of that sample. Table VII-1 shows the response of TA98NR and TA98/1,8-DNP_6, relative to TA98, for several mutagenic atmospheric nitroarenes.

The strains were cultured in 40 mL of L-broth for 12 hours at 37°C with shaking. The culture density was estimated by its absorbance at 550 nm, and each strain was diluted with fresh medium to an absorbance previously calculated to yield the standard culture density of 10^9 colony forming units per mL (approximately 0.28 absorbance units). After dilution, the cultures were maintained in an ice bath for the duration of the test. The titer of each culture was determined by dilution and plating on histidine-supplemented medium E. The standard genotypic markers which were routinely checked were: crystal violet sensitivity, UV sensitivity, and ampicillin resistance. Three standard positive-control mutagens were tested on each strain: 1) 2-nitrofluorene, a positive control mutagen which we have used for the past ten years to check the response of TA98, was also used to check the reduced response of TA98NR relative to TA98; 2) 1,8-dinitropyrene was used to check the reduced response of TA98/1,8-DNP_6 relative to TA98 and TA98NR for nitroarenes which require the Salmonella transacetylase for activation; and 3) quercetin was used to check the equivalent response of these strains to non-nitroarene mutagens. Additionally, benzo(a)pyrene was tested on TA98(+S9) to check the response of this strain to indirect mutagens.

Our testing protocol consistently results in somewhat higher mutagenicities than other laboratories, which we attribute primarily to the use of L-broth instead of Oxoid broth to culture the tester strains. L-broth has about twice the amount of histidine as does Oxoid, and its use results in larger amounts of histidine on the test plate. Because it is the limiting growth factor, a higher amount of histidine results in a

Table VII-1. Response of TA98NR and TA98/1,8-DNP_6 Relative to TA98 for Standard Nitroarenes

Compound	Ratios of Response (-S9)	
	TA98NR to TA98	TA98/1,8-DNP_6 to TA98
2-Nitrofluoranthene	0.24	0.17
3-Nitrofluoranthene	0.49	0.13
8-Nitrofluoranthene	0.33	0.30
1-Nitropyrene	0.13	0.57
2-Nitropyrene	0.10	0.14
1,8-Dinitropyrene	1.0	0.021

higher number of cells on the test plate and hence a higher number of revertants (Maron and Ames 1983). The use of L-broth also results in a somewhat denser background lawn of unreverted Salmonella, but colony morphology and visibility are unaffected.

S9 Mix. Arochlor 1254-induced rat liver S9 was prepared by Litton Bionetics, Inc. according to the method of Ames et al. (1975) and contained 26 mg mL^{-1} protein (manufacturer's analysis). NADP was purchased from Boehringer Mannheim and glucose-6-phosphate was purchased from Sigma Chemical Company.

The S9 mix was prepared by the standard protocol (Ames et al. 1975; Maron and Ames 1983), with 0.01 ml S9 per plate (2% v/v mix). This S9 concentration was chosen since we have previously found a 2% v/v mix to be optimal in activating ambient particulate extracts collected in southern California. Frequently, the use of S9 in testing ambient POM results in a net decrease in activity, as deactivation of direct mutagens overrides the presumed activation of indirect mutagens, such as the PAH. Many nitroarenes are also subject to this S9 suppression of activity.

Testing Protocol. The standard Ames Salmonella plate incorporation mutagenicity test was performed according to the method of Ames and co-workers (Ames et al. 1975, Maron and Ames 1983) with some modifications to improve its accuracy and precision (Belser et al. 1981). Because of the large number of plates required for the complete set of samples, the extracts were assayed in two tests: 1) TA98 with and without S9, and 2) TA98NR and TA98/1,8-DNP_6 without S9. By dividing the tests by strain, the variation in response within one sample set was minimized. Each extract was tested in triplicate at eight doses chosen to logarithmically span the region of linear response observed in the past for ambient POM. In anticipation of lower activities on TA98NR and TA98/1,8-DNP_6, the doses chosen for these strains were twice as great as those for TA98. Hence, each sample was tested at 3, 6, 11, 21, 38, 70, 135, and 250 μg $plate^{-1}$ on TA98 and at 6, 12, 22, 42, 76, 140, 270, and 500 μg $plate^{-1}$ on TA98NR and TA98/1,8-DNP_6.

Each test was performed in a single afternoon by means of a procedure designed to improve intraday precision (Belser et al. 1981). Darkroom conditions were employed throughout to prevent any photodecomposition of the samples which might occur under laboratory fluorescent lights. The plates were incubated at 37°C for 63 hours and counted with a Biotran automatic colony counter (New Brunswick Scientific) directly interfaced to a microcomputer (Apple II). The extract potencies, or specific activities, were obtained by linear regression analysis of the dose-response data in the region of linear response. The slope of the dose-response curve is the specific activity, in revertants μg^{-1}. The ratios of the specific activities on strains TA98NR and TA98/1,8-DNP_6 relative to TA98 were then calculated.

From the specific activities, the extract weights, and the weights of the particulate matter collected, the potencies of the particulate matter, or mutagen loadings in revertants per mg of particulate matter collected, were calculated. Finally, from the specific activities, the extract weights, and the volumes of sampled air, the airborne mutagenicity "concentrations," or mutagen densities in revertants per m^3 of sampled air, were calculated.

C. Results

The complete data set, including the sample collection data, is given in Tables VII-2 to VII-5. The concurrent General Motors Laboratories mutagen density data (J. Siak, T. L. Chan and G. T. Wolff, private communication) are included in Table VII-5 for comparison. As we have observed before in southern California, the sampled POM was principally directly active; the average direct activity (TA98, -S9) was 34.5 rev m^{-3} as compared to 33.2 rev m^{-3} with metabolic activation (TA98, +S9). Figure VII-1 shows the mutagen density with and without S9 observed during this study. The values are intermediate in the range of mutagen densities we have observed before in southern California, and followed a general trend towards higher values at the end of the study. Figure VII-2 shows the TA98 (+S9) to TA98 (-S9) ratio together with the TA98 (-S9) mutagen density, which are anticorrelated. Thus, sampling periods with higher direct mutagenicity tended to be those which exhibited less promutagenicity and greater direct activity. This observation is consistent, in a qualitative manner, with the presence in ambient POM of nitroarenes.

The final nighttime sampling period during this study (8/20-21/86; 2000-0800 PDT) was unusual because of the high levels of volatile and non-volatile nitroarenes present in the atmosphere. For example, the 2-nitrofluoranthene concentration was a factor of ~5 greater than on the previous day and the 1-nitronaphthalene concentration increased by over a factor of two. Concurrent observations of the presence of the nitrate radical indicated that N_2O_5 chemistry could have been occurring on this night. Our measured mutagen density, however, declined by a factor of two, inconsistent with these other observations. Moreover, in contrast to our results, researchers at General Motors Laboratories using CH_2Cl_2 as an extraction solvent observed a significant increase in mutagenicity (TA98, -S9) from the daytime (8/20/86; 0800-2000 PDT) sample to the nighttime (8/20-21/86; 2000-0800 PDT) sample in their tests. Since we had used a benzene-methanol azeotrope as the extraction solvent system, we decided to retest the POM collected during these final two sampling periods using dichloromethane as the extraction solvent.

Table VII-2. Particulate Data for 12-Hour Collections at Citrus College, August 1986

Date	Time of Day (PDT)	Particulate Weight; 2 Filters (mg)	TSP ($\mu g\ m^{-3}$)[a]	Extract Weight (mg)	% Extractable[b]
8/12/86	0800-2000	200.4	130[c]	48.39	24
8/12-13/86	2000-0800	115.6	71	50.28	43
8/13/86	0800-2000	208.8	130	57.61	28
8/13-14/86	2000-0800	134.4	82	59.54	44
8/14/86	0800-2000	233.3	140	64.84	28
8/14-15/86	2000-0800	106.8	65	31.42	29
8/15/86	0800-2000	185.5	110	55.81	30
8/15-16/86	2000-0800	107.3	66	33.61	31
8/16/86	0800-2000	152.6	94	53.66	35
8/16-17/86	2000-0800	96.0	59	46.65	49
8/17/86	0800-2000	134.7	83	52.03	39
8/17-18/86	2000-0800	92.4	57	28.10	30
8/18/86	0800-2000	210.7	130	42.87	20
8/18-19/86	2000-0800	93.7	57	18.81	20
8/19/86	0800-2000	169.5	100	41.08	24
8/19-20/86	2000-0800	97.2	60	36.61	38
8/20/86	0800-2000	188.4	120	49.69	26
8/20-21/86	2000-0800	117.1	72	28.46	24

[a]Flow rates for the two samples (Hi-vols #8 and #11) were 40 scfm for a total sampling volume of 1631 m^3.
[b]16-hr Soxhlet extraction with benzene/methanol (80/20).
[c]Sampling volume ~5% low due to power failure.

Table VII-3. Specific Activities of Particulate Extracts Collected at Citrus College, August 1986

Date	Time of Day (PDT)	Specific Activity (rev μg^{-1})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9	Ratios of Response (-S9) TA98NR to TA98	TA98/ 1,8-DNP_6 to TA98
8/12/86	0800-2000	1.4 (1.8)	1.3 (3.5)	0.58 (2.4)	0.31 (5.8)	0.45	0.24
8/12-13/86	2000-0800	1.0 (2.0)	0.97 (2.2)	0.50 (3.0)	0.21 (7.1)	0.52	0.22
8/13/86	0800-2000	0.77 (1.1)	0.63 (3.2)	0.22 (5.5)	0.093 (8.5)	0.35	0.15
8/13-14/86	2000-0800	1.2 (2.6)	1.2 (1.3)	0.68 (1.4)	0.27 (5.9)	0.57	0.23
8/14/86	0800-2000	0.82 (1.1)	0.87 (4.0)	0.38 (3.2)	0.17 (8.8)	0.44	0.20
8/14-15/86	2000-0800	0.78 (4.0)	0.57 (2.1)	0.34 (2.5)	0.18 (6.1)	0.60	0.32
8/15/86	0800-2000	0.82 (2.1)	0.80 (2.3)	0.31 (3.9)	0.15 (9.3)	0.39	0.19
8/15-16/86	2000-0800	1.5 (0.7)	2.0 (3.1)	1.0 (2.2)	0.47 (4.9)	0.50	0.24
8/16/86	0800-2000	0.84 (2.4)	0.87 (3.4)	0.35 (6.0)	0.15 (13)	0.40	0.17
8/16-17/86	2000-0800	1.4 (2.0)	1.4 (2.9)	0.66 (2.7)	0.29 (2.8)	0.47	0.21
8/17/86	0800-2000	0.86 (2.0)	0.84 (3.1)	0.35 (4.0)	0.14 (14)	0.42	0.17
8/17-18/86	2000-0800	2.3 (1.8)	2.5 (4.0)	1.3 (3.0)	0.55 (3.1)	0.52	0.22
8/18/86	0800-2000	1.6 (1.8)	2.0 (3.3)	0.87 (4.0)	0.29 (5.2)	0.44	0.15
8/18-19/86	2000-0800	1.3 (3.0)	1.1 (2.7)	0.64 (2.8)	0.25 (6.0)	0.58	0.23
8/19/86	0800-2000	1.3 (1.7)	1.4 (5.4)	0.48 (3.1)	0.21 (7.1)	0.34	0.15
8/19-20/86	2000-0800	1.7 (3.2)	1.9 (1.8)	0.81 (2.1)	0.38 (6.3)	0.43	0.20
8/20/86	0800-2000	1.8 (2.6)	2.0 (7.0)	0.69 (3.3)	0.34 (2.6)	0.35	0.17
8/20-21/86	2000-0800	1.6 (2.4)	1.6 (3.3)	0.73 (9.2)	0.31 (4.2)	0.46	0.19

[a]Slope of the dose-response curve in the region of linear response. The number in parentheses is the standard error expressed as a percentage of the specific activity.

Table VII-4. Mutagen Loadings of Particulate Matter Collected at Citrus College, August 1986

Date	Time of Day (PDT)	Mutagen Loading (rev mg^{-1})			
		TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
8/12/86	0800-2000	340	300	140	75
8/12-13/86	2000-0800	430	420	220	91
8/13/86	0800-2000	210	170	61	26
8/13-14/86	2000-0800	530	530	300	120
8/14/86	0800-2000	230	240	110	47
8/14-15/86	2000-0800	230	170	100	53
8/15/86	0800-2000	250	240	93	45
8/15-16/86	2000-0800	470	630	310	150
8/16/86	0800-2000	300	310	120	53
8/16-17/86	2000-0800	680	680	320	140
8/17/86	0800-2000	330	320	140	54
8/17-18/86	2000-0800	700	760	400	170
8/18/86	0800-2000	330	410	180	59
8/18-19/86	2000-0800	260	220	130	50
8/19/86	0800-2000	320	340	120	51
8/19-20/86	2000-0800	640	720	310	140
8/20/86	0800-2000	470	530	180	90
8/20-21/86	2000-0800	390	390	180	75

Table VII-5. Particulate Mutagen Densities, Citrus College, August 1986

Date	Time of Day (PDT)	Mutagen Density (rev m^{-3})[a] TA98 +S9	TA98 -S9	TA98NR -S9	TA98/ 1,8-DNP_6 -S9
8/12/86	0800-2000	42[b]	39[b] (22)[c]	17[b]	9.2[b]
8/12-13/86	2000-0800	31	30 (23)	15	6.5
8/13/86	0800-2000	27	22 (19)	7.8	3.3
8/13-14/86	2000-0800	44	44 (11)	25	10
8/14/86	0800-2000	33	35 (21)	15	6.8
8/14-15/86	2000-0800	15	11 (9)	6.5	3.5
8/15/86	0800-2000	28	27 (15)	11	5.1
8/15-16/86	2000-0800	31	41 (13)	21	10
8/16/86	0800-2000	28	29 (14)	12	4.9
8/16-17/86	2000-0800	40	40 (27)	19	8.3
8/17/86	0800-2000	27	27 (13)	11	4.5
8/17-18/86	2000-0800	40	43 (22)	22	9.5
8/18/86	0800-2000	42	53 (17)	23	7.6
8/18-19/86	2000-0800	15	13 (18)	7.4	2.9
8/19/86	0800-2000	33	35 (12)	12	5.3
8/19-20/86	2000-0800	38	43 (16)	18	8.5
8/20/86	0800-2000	55	61 (24)	21	10
8/20-21/86	2000-0800	28	28 (38)	13	5.4

[a]Flow rates for the two samples (Hi-vols #8 and #11) were 40 SCFM for a total sampling volume of 1631 m^3.
[b]Sampling volume ~5% low due to power failure.
[c]Data in parenthesis from General Motors Laboratories (see text).

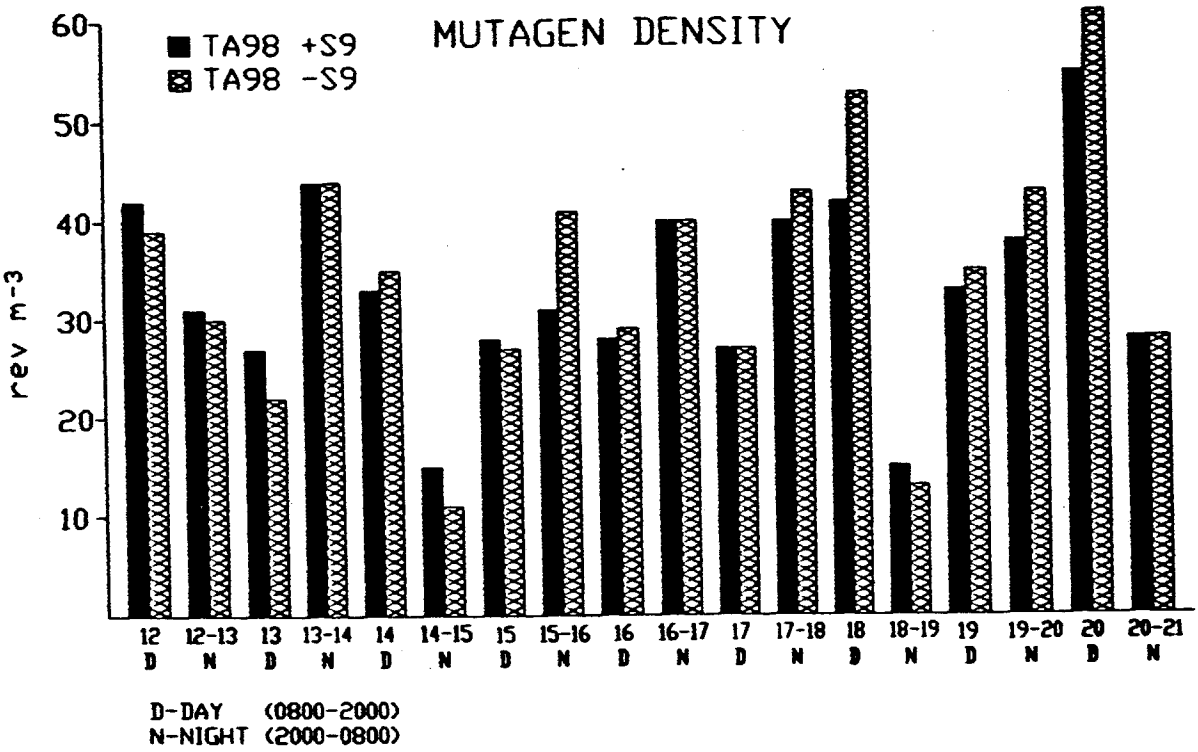


Figure VII-1. 12-Hour particulate mutagen densities at Citrus College, Glendora, CA, August 12-21, 1986.

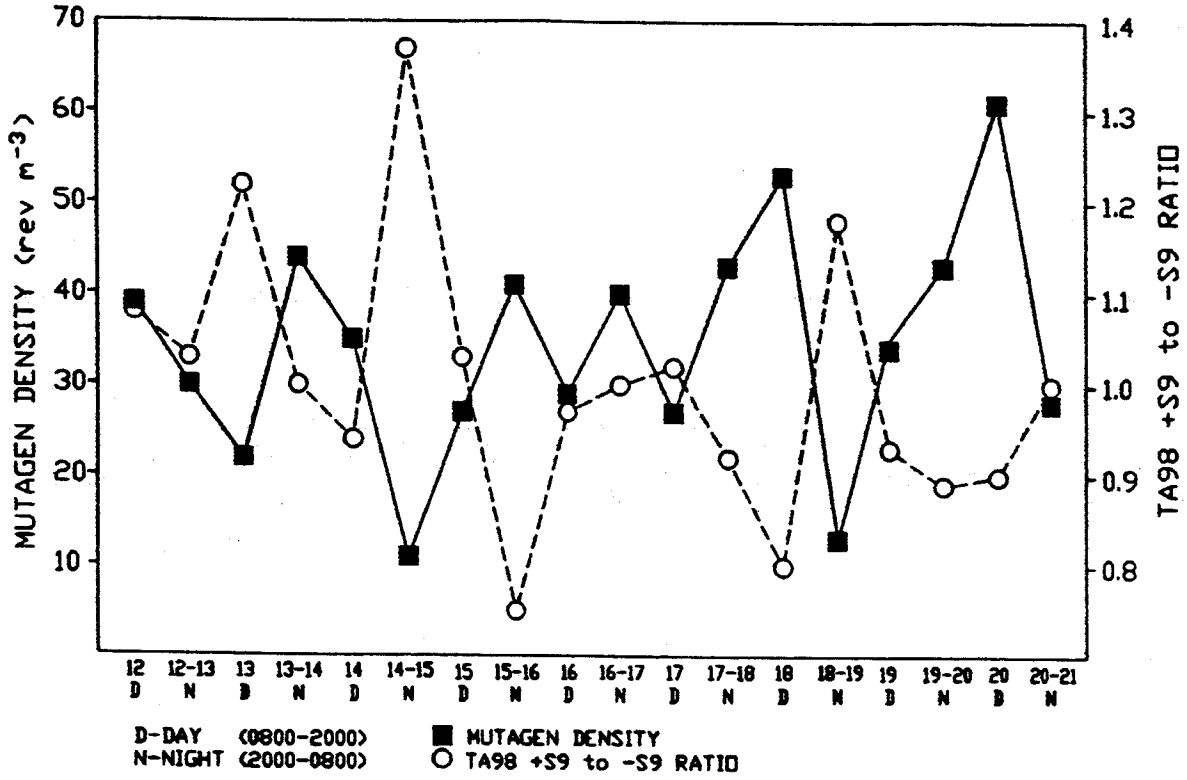


Figure VII-2. Mutagen density (TA98, -S9) vs. the +S9 to -S9 ratio for August 12-21, 1986, Glendora, CA.

For this second mutagenicity test using CH_2Cl_2-extraction, POM collected on TIGF filters in Hi-vol samplers modified to allow PUF plugs to be placed downstream from the filters was employed. These modified Hi-vol samplers were operated at a flow rate of 23 SCFM (instead of the conventional 40 SCFM) to ensure that the flow controller remained operative. One filter from the daytime (8/20/86; 0800-2000 PDT) and one filter from the nighttime (8/20-21/86; 2000-0800 PDT) collection period were Soxhlet extracted for 16 hours with CH_2Cl_2, and tested on TA98 (-S9).

The results of this collection and mutagenicity test are given in Table VII-6, together with the data for our previous test of the benzene-methanol extracts. As can be seen from the TSP data, the modified samplers collected more particulate matter than the standard Hi-vol, as expected since these Hi-vols were not equipped with a size-selective inlet. This was not expected to have greatly affected the mutagenicity results, however, because very little mutagenicity is present on particles larger than ~10 μ.

Table VII-6. The Effect of Extraction Solvent on Mutagenicity

	Benzene-Methanol Extracts		CH_2Cl_2 Extracts	
Date	8/20/86	8/20-21/86	8/20/86	8/20-21/86
Time Period (PDT)	Day 0800-2000	Night 2000-0800	Day 0800-2000	Night 2000-0800
Flow Rate (SCFM)	40.0	40.0	23.0	23.0
TSP ($\mu g\ m^{-3}$)	120	72	160	110
% Extractable	26	24	12	14
Specific Activity (rev μg^{-1})	2.0	1.6	2.5	5.5
Mutagen Loading (rev mg^{-1})	530	390	300	760
Mutagen Density (rev m^{-3})	61	28	47	83

The more polar benzene-methanol solvent system extracted much more material than did CH_2Cl_2. Despite the larger amount of polar material present in the benzene-methanol samples, the mutagen density for the nighttime sample is three-fold lower than for the corresponding CH_2Cl_2-extracted sample. In contrast, the mutagen density for the benzene-methanol daytime sample is somewhat higher than for the corresponding CH_2Cl_2-extracted sample. Apparently, the polar material in the benzene-methanol extract of the nighttime sample inhibited the mutagenicity of this extract, probably through toxic or bacteriostatic action. In contrast, the mutagenicity of the polar compounds in the daytime sample overcame any inhibitory effect.

These observations illustrate the inherent compromises in choosing a solvent system for extracting ambient POM. The benzene-methanol solvent system was chosen precisely because it extracts more polar material than does CH_2Cl_2 and does not generate the artifactual mutagenicity associated with the use of acetonitrile. Indeed, because inhibitory compounds may be of the same polarity as mutagens, every solvent system must result in an underestimation of the mutagenicity of ambient POM. This underscores the need for identification and quantification of ambient mutagens. Once identified and tested for mutagenicity in their pure form, the known mutagens in a sample can be quantified and an accurate sum of their mutagenicities can be obtained.

VIII. CONCLUSIONS

The objectives of SAPRC's involvement in the ARB-funded CSMCS study held at Citrus College, Glendora, CA, during the period August 12-21, 1986, were met. Using long pathlength differential optical absorption and Fourier transform infrared absorption spectroscopic techniques, the ambient concentrations of NO_2, HONO, HCHO, HNO_3, NH_3 and the NO_3 radical were monitored in an essentially continuous mode throughout this study period. Since these data were obtained using absolute, in-situ, spectroscopic methods, they have served as benchmark data for the evaluation of other, more portable, measurement methods for the determination of HCHO and HNO_3 concentrations during the SCAQS carried out in 1987.

Based upon the experimental methods used and ambient air concentration data obtained in our recent study at El Camino Community College, Torrance, we were able to employ a complementary set of sampling techniques to provide a comprehensive data set concerning the ambient atmospheric concentrations of both volatile and non-volatile PAH and nitroarenes during this study at Citrus College. Ambient atmospheric concentration data were obtained for the following PAH: naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benz(a)-anthracene, chrysene/triphenylene and benzo(a)pyrene, and the following nitroarenes: 1- and 2-nitronaphthalene, 3-nitrobiphenyl, 2-, 3- and 8-nitrofluoranthene and 1- and 2-nitropyrene. The ambient concentrations of the PAH cover a very large range (>1000) with the most volatile PAH, naphthalene, being the most abundant. Indeed, the naphthalene concentration exceeded 1 ppb during the 12-hr nighttime period 2000-0800 PDT on August 20-21, and averaged 0.7 ppb (3700 ng m^{-3}) over the entire study period. The next most abundant PAH were the 1- and 2-methylnaphthalenes, with 2-methylnaphthalene being about twice as abundant as 1-methylnaphthalene.

The ambient concentrations of the PAH exhibited diurnal variations, with the concentrations generally being higher during the nighttime sampling periods than during the daytime periods. This diurnal variation can most readily be seen for the volatile PAH which were sampled onto the high and low flow Tenax cartridges and for which individual 12-hr analyses were carried out. This diurnal variation could, in general, be due to

differing day/night emission rates, meteorology (with lower inversion heights and hence higher concentrations during the nighttime periods) and/or differing atmospheric removal rates due to chemical reactions. The observation (Table VI-1) that the magnitude of the diurnal variation depended on the specific PAH, with the largest variations being for the most chemically reactive PAH, indicates that part of this variation was due to chemical removal of the PAH during daytime hours.

The 2-3 ring PAH monitored using the Tenax cartridge system all react with the OH radical during daylight hours (Atkinson 1986, Atkinson and Aschmann 1987b), with expected lifetimes due to this OH radical reaction of approximately 3 days for biphenyl and fluorene and 2-12 hrs for the other PAH. The PAH naphthalene, 1- and 2-methylnaphthalene, acenaphthene, acenaphthylene and phenanthrene also react, to a lesser extent, with N_2O_5. In addition, acenaphthene and acenaphthylene also react with NO_3 radicals (Atkinson and Aschmann 1987b). These N_2O_5 and/or NO_3 radical removal processes were likely to be of minor significance during this study, since the NO_3 radical (and hence N_2O_5) concentrations were low. In addition, acenaphthylene reacts with O_3 (Atkinson and Aschmann 1987b), with this removal process again being most important during daytime. Interestingly, the ratio (average nighttime concentration/average daytime concentration) correlates well with the OH radical reaction rate constant (which varies from 7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for biphenyl to 1.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for acenaphthylene (Atkinson 1986, Atkinson and Aschmann 1987b), as shown by the plot in Figure VIII-1. This good correlation confirms our expectation that daytime reaction with the OH radical is an important atmospheric removal process for the PAH present in the gas phase.

The nitroarenes also exhibit a diurnal concentration profile, as shown in Figure VIII-2 which gives our earlier data from Torrance, CA (Winer et al. 1987) as well as from Citrus College. Again, this observed diurnal variation in the nitroarene concentrations can be due to differing emission rates, differing formation rates from their parent PAH during transport through the atmosphere, meteorology, or differing removal rates during daytime and nighttime periods. Our data for the PAH (Figure VIII-1) show that meteorology at Citrus College had a relatively minor effect, of the order of 20% (estimated from the intercept representing no OH radical

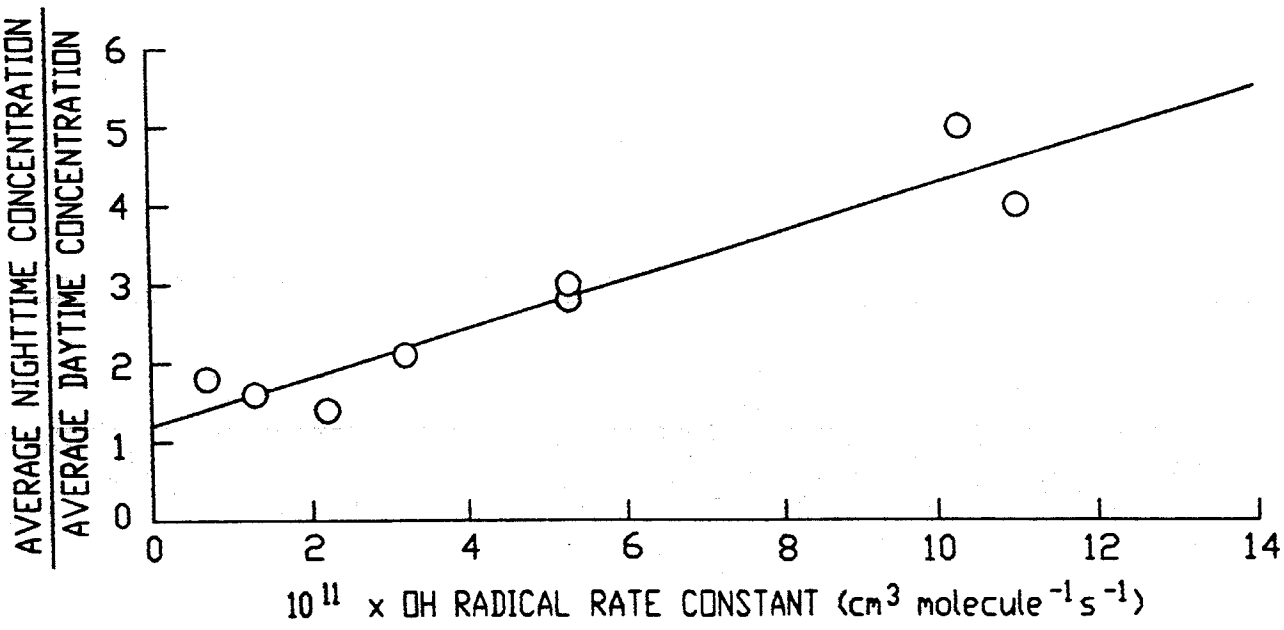


Figure VIII-1. Plot of the average nighttime/average daytime concentration ratio for the volatile PAH against the OH radical reaction rate constant.

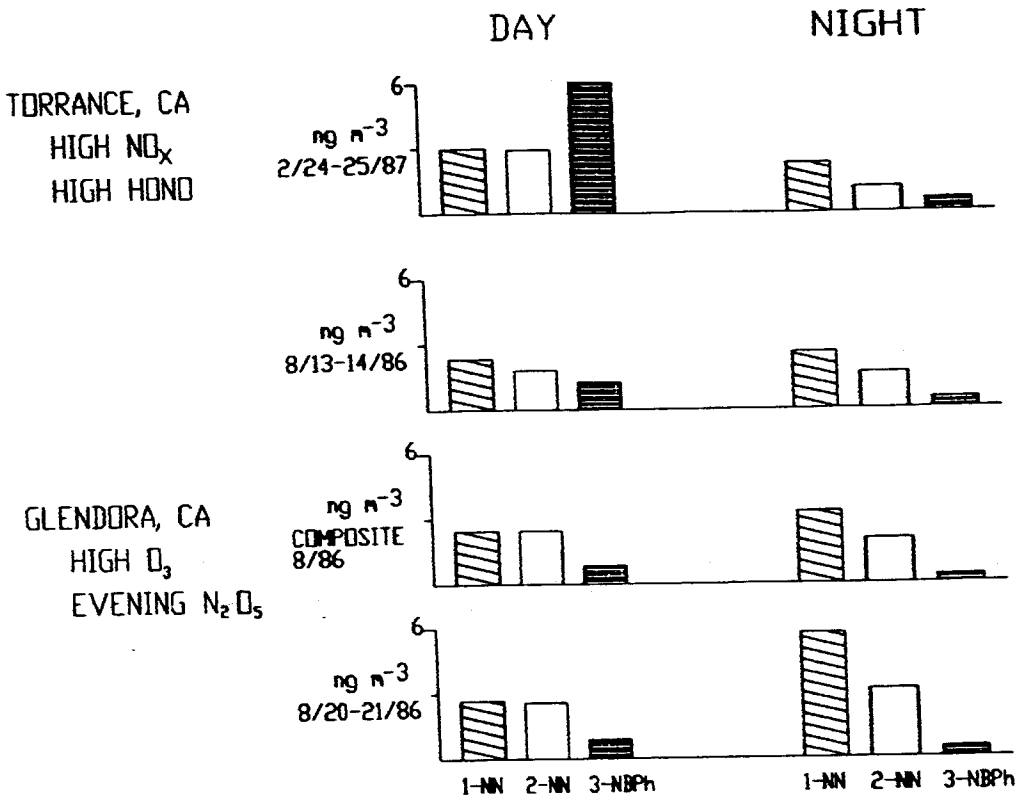


Figure VIII-2. Comparison of the daytime and nighttime ambient concentrations of 1-nitronaphthalene (1-NN), 2-nitronaphthalene (2-NN) and 3-nitrobiphenyl (3-NBPh) at El Camino Community College, Torrance, CA (Winer et al. 1987) and Citrus College, Glendora.

reaction), on the day/night concentration ratio. Further, it is expected (Atkinson et al. 1987) that the atmospheric OH radical reactions of the nitroarenes will be relatively slow. Hence, since 3-nitrobiphenyl is not expected to be emitted and the daytime/nighttime emission rates of the nitronaphthalenes are not likely to vary significantly, the observed differences in the day/night concentration profiles for 1- and 2-nitronaphthalene and 3-nitrobiphenyl strongly suggest differing formation rates. In particular, our observation that the daytime concentrations of 3-nitrobiphenyl are always higher than the nighttime concentration (in total contrast to the situation for the PAH) shows that 3-nitrobiphenyl must be made in the atmosphere during daytime hours. Indeed, we have shown from laboratory studies (Atkinson et al. 1987) that the daytime OH radical reaction with biphenyl (the only significant atmospheric chemical removal process for biphenyl) forms 3-nitrobiphenyl in approximately 5% yield. 1- and 2-Nitronaphthalene are also formed from the reaction of OH radicals with naphthalene (Atkinson et al. 1987), but these nitroarenes can also be formed from the nighttime reaction of naphthalene with N_2O_5 (Atkinson et al. 1987).

In our previous study in Torrance, CA, (Winer et al. 1987) NO_3 radicals were not present during nighttime hours, and hence the N_2O_5 formation route to the 1- and 2-nitronaphthalenes was not operative, and the daytime concentrations of the 1- and 2-nitronaphthalenes and 3-nitrobiphenyl were higher than during the nighttime, as expected from a daytime formation pathway via OH radical reaction from their parent PAH. In contrast, at Citrus College NO_3 radicals were observed on several evenings, and both daytime and nighttime formation of 1- and 2-nitronaphthalene was hence possible (note that 3-nitrobiphenyl could only be formed during the daytime). Indeed, while the daytime 3-nitrobiphenyl concentrations were higher than the nighttime concentrations, the 1- and 2-nitronaphthalene concentrations were as high, or higher, during the nights. Even more interesting is the observation that during daytime the 1- and 2-nitronaphthalene concentrations were comparable, consistent with the similar formation yields from the daytime OH radical-initiated reactions with naphthalene (Atkinson et al. 1987). During nighttime, however, the 1-nitronaphthalene concentrations were significantly higher than the 2-nitronaphthalene concentrations, consistent with nighttime formation

from N_2O_5 reaction with naphthalene, for which the 1- and 2-nitronaphthalene yields are 15% and 7%, respectively (Atkinson et al. 1987).

The ambient nitroarene concentrations also vary widely from compound to compound, and, as with the PAH, the most volatile nitroarenes are again the most abundant. Indeed, as shown in Table VIII-1, the ambient atmospheric concentrations of 1- and 2-nitronaphthalene and 3-nitrobiphenyl (measured at both Torrance (Winer et al. 1987) and Citrus College) are comparable to the ambient concentrations of fluoranthene and (not shown) pyrene, and are generally an order of magnitude higher than the concentrations of 2-nitrofluoranthene, the most abundant particle-associated nitroarene.

As noted in previous sections of this report, the PAH themselves are not directly mutagenic in the Ames assay without microsomal activation. The ambient atmospheric concentrations of the particle-associated nitroarenes (which are direct-acting mutagens), when combined with their mutagenic activities (Table VII-1), allow the ambient mutagenic densities resulting from the nitrofluoranthenes and nitropyrenes (by far the most abundant particle-associated nitroarenes) to be calculated. Table VIII-2 gives the overall direct-acting mutagenic densities towards strain TA98 (-S9) calculated from our measured ambient concentrations of 2-, 3-, and 8-nitrofluoranthene and 1- and 2-nitropyrene for the six time-periods for which data were obtained. The mutagenic densities (rev m^{-3}) calculated from the measured ambient concentrations of these nitrofluoranthenes and nitropyrenes ranged from approximately 1-9 rev m^{-3}. 2-Nitrofluoranthene itself accounted for from 50-90% of this overall mutagenic density contributed by the nitroarenes of molecular weight 247.

These calculated nitrofluoranthene and nitropyrene mutagen densities account for typically 10% of the measured ambient mutagenicity. It is difficult to cite a definite numerical contribution of the nitrofluoranthenes and nitropyrenes to ambient mutagenicity due to potential problems in the Ames assay, as discussed in Section VII above. This 10% figure for the contribution of the particle-associated nitroarenes to ambient mutagenicity is consistent with the values given by Arey et al. (1988), and shows that the majority, i.e. typically 90%, of the mutagenicity of ambient POM is presently unaccounted for. This, as yet unaccounted for direct-acting mutagenicity could be associated with other PAH-

derivatives formed in the atmosphere during transport from source to receptor or from other classes of organics. Further work to attempt to determine the identity of these other mutagens and their sources (direct emissions versus atmospheric formation) is clearly necessary.

Table VIII-1. Ambient Atmospheric Concentrations (ng m^{-3}) of Selected PAH and Nitroarenes at Torrance and Glendora, CA

Location and Date	Concentration (ng m^{-3})				
	1-Nitro-naphthalene	2-Nitro-naphthalene	3-Nitro-biphenyl	Fluor-anthene	2-Nitro-fluoranthene
Torrance, CA 2/25/86 0600-1800 hr[a]	3.0	2.9	6.0	8.0	0.3
Torrance, CA 2/24-25/86 1800-0600 hr[a]	2.3	1.1	0.6	9.7	0.3
Glendora, CA 8/21/86 0800-2000 hr[b]	2.7	2.6	0.9	5.9	0.4
Glendora, CA 8/20-21/86 2000-0800 hr[b]	5.7	3.1	0.5	6.8	2.0

[a]Times in PST.
[b]Times in PDT.

Table VIII-2. Mutagenic Densities (rev m^{-3}) Towards TA98(-S9) at Citrus College, Glendora Due to the Measured Ambient Concentrations of 2-, 3- and 8-Nitrofluoranthene and 1- and 2-Nitropyrene (Using the Mutagenicity Data given in Table VII-1 for the Mutagenic Activities of these Nitroarenes)

Sample #	Date and Time (PDT)	Rev m^{-3}
1	8/13/86 0800-2000 hr	1.4
2	8/13-14/86 2000-0800 hr	2.7
3	8/15,16,17,18/86 Day composite, 0800-2000 hr	1.7
4	8/15-16, 16-17, 17-18, 18-19/86 Night Composite, 2000-0800 hr	5.2
5	8/20/86 0800-2000 hr	2.1
6	8/20-21/86 2000-0800 hr	9.4

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APPENDIX A

DOAS Measurements of Gaseous Nitrous Acid (HONO), Formaldehyde (HCHO) and Nitrogen Dioxide (NO_2) at Citrus College, Glendora, from August 12-21, 1986

Table A-1. Ambient Concentrations Determined by DOAS During Citrus College Study

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
13-AUG-86	00:14-00:33	2.1	7.9	65.0
	00:33-00:47	1.8	6.7	63.7
	01:08-01:22	1.9	7.8	62.3
	01:22-01:36	2.0	7.0	64.2
	01:56-02:10	2.3	6.8	59.6
	02:10-02:24	2.2	6.4	60.9
	02:45-02:59	2.4	6.4	55.8
	02:59-03:13	2.4	7.8	56.8
	03:34-03:48	2.8	5.3	52.4
	03:48-04:02	1.9	6.5	55.7
	04:22-04:37	1.9	5.5	54.7
	04:37-04:51	3.2	5.6	47.6
	05:11-05:25	3.1	7.3	49.1
	05:25-05:39	3.7	5.3	46.0
	06:00-06:14	4.1	6.6	44.1
	06:14-06:28	3.0	7.4	49.9
	06:49-07:03	3.5	5.9	46.3
	07:03-07:17	3.1	7.8	52.3
	07:37-07:51	2.0	10.0	65.7
	07:51-08:06	1.5	10.8	74.2
	08:11-08:31	1.1	11.0	73.0
	08:31-08:46	1.3	9.7	76.3
	08:46-09:01	1.2	12.5	87.3
	09:01-09:16	0.9	10.7	91.7
	09:16-09:31	0.8	12.6	91.7
	09:31-09:46	ND[a]	12.2	97.5
	09:46-10:01	ND	14.0	93.8
	10:01-10:16	ND	13.0	89.3
	10:16-10:31	ND	14.2	83.2
	10:31-10:46	ND	11.9	78.0
	10:46-11:01	ND	11.6	72.5
	11:01-11:16	ND	11.4	66.2
	11:16-11:31	ND	12.2	57.7
	11:31-11:46	ND	11.3	53.5
	11:46-12:01	ND	11.5	49.3
	12:01-12:16	ND	11.0	43.8
	12:16-12:31	ND	13.1	43.7
	12:31-12:46	ND	13.3	41.2
	12:46-13:01	ND	11.3	44.0
	13:01-13:16	ND	11.8	48.7
	13:16-13:31	ND	10.0	43.8
	13:31-13:46	ND	14.9	40.2
	13:46-14:01	ND	13.1	35.5

(continued)

Table A-1 (continued) - 2

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
13-AUG-86	15:46-16:01	ND	15.8	37.1
	16:01-16:16	ND	14.0	38.1
	16:16-16:31	ND	14.4	38.4
	16:31-16:46	ND	15.7	35.8
	16:46-17:01	ND	15.4	43.2
	17:01-17:16	ND	16.0	36.9
	17:16-17:31	ND	14.8	41.1
	17:31-17:46	ND	13.7	43.1
	17:46-17:53	ND	13.2	47.4
	18:00-18:17	ND	10.7	52.8
	18:17-18:32	ND	11.0	53.9
	18:32-18:47	ND	9.5	52.7
	19:10-19:21	ND	9.4	61.4
	19:42-19:53	ND	9.6	62.2
	20:15-20:26	ND	9.1	67.9
	20:50-21:01	0.8	9.1	73.0
	21:22-21:33	ND	6.8	76.1
	22:37-22:49	1.8	8.5	73.7
	23:21-23:35	2.2	6.8	71.4
	23:35-23:49	1.9	6.6	68.2
14-AUG-86	00:10-00:24	1.6	7.4	67.3
	00:24-00:38	1.9	5.4	65.8
	00:58-01:12	2.0	6.1	67.8
	01:12-01:26	2.1	5.9	64.2
	01:47-02:01	2.4	5.8	60.5
	02:01-02:15	2.3	5.9	61.7
	02:36-02:50	2.5	5.2	59.6
	02:50-03:04	2.0	ND	63.1
	03:25-03:39	2.0	6.4	63.6
	03:39-03:53	2.0	4.9	65.2
	04:13-04:27	3.1	6.1	60.5
	04:27-04:41	2.3	5.5	62.5
	05:02-05:16	2.5	ND	60.9
	05:16-05:30	2.5	7.0	62.8
	05:51-06:05	2.7	ND	60.9
	06:05-06:19	2.9	4.8	60.9
	06:40-06:54	2.5	7.9	65.1
	06:54-07:08	2.5	5.4	60.0
	07:28-07:42	2.1	8.0	61.5
	07:42-07:56	1.5	7.6	68.8
	08:18-08:33	1.3	11.0	70.7
	08:33-08:48	0.9	13.4	77.4
	08:48-09:03	ND	11.2	81.8
	09:03-09:18	ND	12.1	79.2

(continued)

Table A-1 (continued) - 3

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
14-AUG-86	09:18-09:33	ND	14.2	68.6
	09:48-10:03	ND	12.5	79.9
	10:03-10:18	ND	13.6	73.2
	10:33-10:48	ND	14.0	65.7
	10:48-11:03	ND	14.4	63.7
	11:03-11:18	ND	13.3	47.8
	11:18-11:33	ND	13.6	55.9
	11:33-11:48	ND	13.4	50.2
	12:18-12:33	ND	13.3	27.8
	12:33-12:48	ND	11.6	44.7
	12:48-13:03	ND	12.7	50.2
	13:03-13:18	ND	14.4	37.5
	13:18-13:33	ND	8.8	33.2
	13:33-13:48	ND	10.1	29.0
	13:48-14:03	ND	11.6	28.8
	14:03-14:14	ND	7.8	23.0
	15:06-15:21	ND	13.8	26.2
	15:21-15:36	ND	16.4	26.2
	15:36-15:51	ND	14.7	30.7
	16:08-16:23	ND	13.4	40.4
	16:23-16:38	ND	15.0	39.7
	16:38-16:53	ND	12.5	39.6
	17:09-17:24	ND	13.8	39.6
	17:24-17:43	ND	12.9	40.0
	17:43-18:00	ND	11.1	44.6
	18:00-18:15	ND	10.1	45.8
	18:15-18:35	ND	11.7	46.8
	19:18-19:38	ND	10.4	56.7
	19:59-20:10	ND	9.6	62.2
	20:31-20:42	ND	8.3	80.5
	21:02-21:14	1.2	8.1	79.7
	21:28-21:43	1.3	7.2	77.2
	22:22-22:36	1.2	6.3	74.4
	22:36-22:50	1.3	6.0	72.6
	23:10-23:24	1.4	6.0	62.2
	23:24-23:38	1.6	5.7	57.4
15-AUG-86	00:00-00:14	1.6	5.6	54.6
	00:14-00:28	1.5	5.3	55.7
	00:48-01:02	1.5	5.7	53.9
	01:02-01:16	1.7	5.4	53.0
	01:36-01:50	1.8	6.3	51.2
	01:50-02:04	1.2	5.9	51.9
	02:25-02:39	1.9	5.9	48.9
	02:39-02:53	1.9	6.2	47.8

(continued)

Table A-1 (continued) - 4

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
15-AUG-86	03:14-03:28	1.9	5.3	42.7
	03:28-03:42	2.0	5.4	42.0
	04:02-04:16	2.0	5.7	42.1
	04:16-04:30	2.1	5.9	39.8
	04:51-05:05	2.4	5.3	38.9
	05:05-05:19	2.6	5.6	39.6
	05:39-05:53	1.9	6.2	41.6
	05:53-06:07	1.9	6.5	43.5
	06:28-06:42	2.3	4.7	39.8
	06:42-06:56	1.9	8.1	46.7
	07:17-07:31	1.7	7.2	51.2
	07:31-07:45	1.8	7.8	51.8
	07:55-08:09	1.2	8.6	57.2
	08:10-08:25	1.2	8.6	61.1
	08:25-08:40	1.3	8.0	60.0
	08:40-08:55	1.4	9.6	63.6
	08:55-09:10	1.1	10.4	65.3
	09:25-09:40	ND	9.8	66.5
	09:40-09:55	ND	10.2	62.9
	09:55-10:10	ND	11.6	63.7
	10:10-10:25	0.9	10.8	58.3
	10:25-10:40	ND	12.0	60.8
	10:40-10:58	ND	12.2	61.9
	10:58-11:13	ND	13.5	57.5
	11:13-11:29	ND	13.2	57.4
	11:29-11:43	ND	12.0	51.9
	11:43-11:58	ND	13.4	47.4
	11:58-12:13	ND	12.8	39.7
	12:13-12:28	ND	12.2	39.3
	12:28-12:43	ND	12.9	39.9
	12:43-12:58	ND	12.9	36.1
	12:58-13:18	ND	12.9	31.3
	13:18-13:34	ND	13.5	28.3
	13:34-13:49	ND	11.3	31.6
	13:49-14:04	ND	14.1	34.3
	14:04-14:19	ND	18.9	30.2
	14:19-14:34	ND	15.8	24.8
	14:34-14:49	ND	14.4	21.6
	14:49-15:04	ND	15.9	24.7
	15:04-15:19	ND	16.8	29.9
	15:19-15:34	ND	15.0	35.9
	15:34-15:54	ND	13.7	45.8
	15:55-16:13	ND	12.0	43.6
	16:13-16:28	ND	11.4	45.4
	16:28-16:43	ND	10.4	47.2

(continued)

Table A-1 (continued) - 5

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
15-AUG-86	18:58-19:14	ND	7.7	59.9
	19:30-19:46	ND	7.5	72.8
	20:59-21:14	1.2	4.5	63.3
	21:30-21:53	1.4	5.3	60.0
	22:15-22:33	1.5	4.7	59.8
	23:03-23:22	2.0	6.2	61.1
	23:22-23:36	1.5	6.6	60.3
	23:52-24:00	2.1	4.8	60.6
16-AUG-86	00:00-00:02	2.1	4.8	60.6
	00:16-00:22	2.0	7.1	56.7
	00:34-00:49	2.3	5.4	56.7
	00:49-01:04	2.7	5.4	55.2
	01:04-01:19	2.9	6.9	54.1
	01:19-01:34	3.6	8.4	48.5
	01:34-01:49	3.3	7.8	50.4
	01:49-02:04	3.4	6.6	49.0
	02:04-02:19	2.7	5.9	53.7
	02:19-02:34	3.0	4.7	52.6
	02:34-02:49	2.8	4.5	51.6
	02:49-03:04	3.1	6.3	50.4
	03:04-03:19	2.8	7.7	52.6
	03:19-03:34	3.2	6.2	47.5
	03:34-03:49	2.9	6.0	49.5
	03:49-04:04	2.6	5.6	51.9
	04:04-04:19	3.0	7.1	46.5
	04:19-04:34	3.6	4.7	46.0
	04:34-04:48	3.5	7.2	47.2
	04:48-05:03	3.5	6.6	45.4
	05:03-05:18	3.5	7.1	46.9
	05:18-05:33	3.5	5.6	45.0
	05:33-05:48	3.5	7.2	46.0
	05:48-06:03	3.5	6.9	46.8
	06:03-06:18	2.9	ND	46.9
	06:18-06:37	3.3	7.2	44.9
	06:37-06:54	3.6	6.2	38.5
	06:54-07:11	3.2	5.7	39.4
	07:11-07:28	2.9	6.9	45.1
	07:28-07:47	2.2	8.3	51.9
	07:47-08:02	1.3	7.7	59.6
	08:02-08:17	1.6	7.1	70.5
	08:17-08:32	0.9	8.1	73.6
	08:32-08:47	1.2	9.5	71.1
	08:47-09:02	0.9	10.4	65.4
	09:02-09:17	ND	9.2	68.1

(continued)

Table A-1 (continued) - 6

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
16-AUG-86	09:17-09:32	0.8	10.7	70.7
	09:32-09:47	ND	12.6	71.0
	09:47-10:02	0.9	12.6	62.9
	10:02-10:17	ND	8.7	61.9
	10:17-10:32	ND	9.9	61.5
	10:32-10:47	ND	13.1	59.8
	10:47-11:01	ND	12.5	59.0
	11:01-11:16	ND	12.6	54.3
	11:16-11:31	ND	13.5	52.6
	11:31-11:46	ND	13.1	41.6
	11:46-12:01	ND	11.3	38.4
	12:01-12:18	ND	9.6	33.7
	12:18-12:33	ND	11.7	30.8
	12:33-12:48	ND	12.9	24.2
	12:48-13:03	ND	8.1	19.3
	13:03-13:18	ND	10.1	14.3
	13:18-13:33	ND	11.9	16.0
	13:33-13:48	ND	9.6	13.1
	13:48-14:03	ND	8.4	12.8
	14:03-14:18	ND	14.0	14.1
	14:18-14:34	ND	10.4	11.8
	14:34-14:49	ND	10.2	13.2
	14:49-15:04	ND	10.4	13.7
	15:04-15:19	ND	11.6	11.8
	15:19-15:34	ND	11.7	15.4
	15:34-15:49	ND	11.3	15.4
	15:49-16:04	ND	11.4	14.4
	16:04-16:19	ND	10.2	16.3
	16:19-16:34	ND	11.7	19.4
	16:34-16:52	ND	13.7	21.4
	16:52-17:07	ND	12.6	23.6
	17:09-17:27	ND	11.3	28.2
	17:27-17:42	ND	11.3	35.5
	17:42-17:57	ND	9.6	37.1
	17:57-18:12	ND	10.8	36.7
	18:12-18:27	ND	10.1	38.9
	18:27-18:43	ND	9.2	38.1
	18:59-19:15	ND	6.8	52.0
	19:35-19:46	ND	8.3	64.2
	20:08-20:19	1.4	8.1	75.4
	20:40-20:51	1.5	8.4	77.9
	21:12-21:23	1.7	7.8	83.3
	21:43-21:54	1.7	8.6	81.1
	22:14-22:26	2.0	6.8	65.0
	22:48-23:02	2.0	6.3	73.0

(continued)

Table A-1 (continued) - 7

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
16-AUG-86	23:02-23:16	2.0	5.0	68.1
	23:37-23:51	2.1	6.6	66.7
	23:51-24:00	2.4	6.2	66.2
17-AUG-86	00:00-00:05	2.4	6.2	66.2
	00:25-00:39	2.7	8.1	58.2
	00:40-00:54	3.2	10.4	64.6
	01:14-01:28	3.7	8.9	62.8
	01:28-01:42	3.6	8.7	64.3
	02:03-02:17	3.8	8.3	60.8
	02:17-02:31	4.0	8.0	60.4
	02:52-03:05	3.7	9.3	53.9
	03:05-03:20	2.6	8.4	47.8
	03:40-03:54	3.0	9.0	34.5
	03:54-04:08	1.9	9.2	23.7
	04:29-04:43	2.5	6.5	26.7
	04:43-04:57	2.4	6.6	30.4
	05:18-05:32	1.5	6.6	21.9
	05:32-05:46	1.7	8.4	23.7
	06:06-06:20	1.6	6.9	18.7
	06:20-06:34	1.7	6.0	19.0
	06:55-07:09	1.5	8.0	24.2
	07:09-07:23	1.2	9.2	28.1
	07:45-08:00	ND	8.6	18.2
	08:10-08:25	ND	8.3	21.5
	08:25-08:40	ND	10.1	25.1
	08:40-08:55	ND	10.2	33.6
	08:55-09:09	ND	13.1	36.8
	09:09-09:24	ND	14.1	45.9
	09:24-09:39	ND	16.1	50.4
	09:39-09:54	ND	13.8	52.3
	09:54-10:09	ND	14.7	56.6
	10:09-10:24	ND	12.5	48.0
	10:24-10:39	ND	16.2	42.2
	10:39-10:54	ND	17.3	39.7
	12:45-13:00	ND	14.3	20.1
	13:00-13:15	ND	13.4	16.0
	13:15-13:30	ND	13.4	18.3
	13:30-13:45	ND	12.6	15.2
	13:45-14:00	ND	12.9	17.6
	14:00-14:15	ND	12.5	16.0
	14:15-14:30	ND	12.2	13.2
	14:30-14:45	ND	12.0	11.3
	14:45-15:00	ND	11.9	10.6
	15:00-15:15	ND	11.4	11.7

(continued)

Table A-1 (continued) - 8

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
17-AUG-86	15:15-15:30	ND	15.3	15.3
	15:30-15:45	ND	14.4	22.3
	15:45-16:00	ND	14.6	21.5
	16:00-16:17	ND	14.6	22.3
	16:17-16:32	ND	13.7	22.5
	16:32-16:47	ND	11.0	22.4
	16:47-17:02	ND	7.7	20.2
	17:02-17:17	ND	8.0	21.0
	17:17-17:32	ND	8.1	24.4
	17:32-17:47	ND	7.2	26.8
	17:47-18:02	ND	8.6	33.7
	18:02-18:17	ND	6.0	40.5
	18:17-18:32	ND	7.5	51.4
	18:32-18:47	ND	5.3	51.1
	18:47-19:02	ND	9.8	58.9
	19:02-19:17	ND	7.7	63.5
	19:43-19:54	ND	8.7	78.9
	20:15-20:26	1.2	8.3	81.8
	20:47-20:58	ND	7.2	77.4
	21:19-21:30	1.2	5.4	69.8
	21:51-22:02	1.0	6.8	70.6
	22:23-22:34	1.0	7.2	69.5
	22:55-23:06	ND	7.2	65.7
	23:30-23:41	1.1	7.7	69.7
	23:41-23:55	1.3	6.2	76.2
18-AUG-86	00:18-00:30	1.4	5.7	75.1
	00:30-00:44	1.9	5.7	69.6
	01:05-01:19	1.8	6.0	76.0
	01:19-01:33	1.7	6.8	76.0
	01:53-02:07	2.1	6.9	73.5
	02:07-02:21	2.1	7.2	75.7
	02:42-02:56	1.5	8.0	75.2
	02:56-03:10	1.7	7.8	72.7
	03:31-03:45	2.3	8.9	69.5
	03:45-03:59	1.9	8.6	67.4
	04:20-04:34	2.5	8.9	65.9
	04:34-04:48	2.8	5.1	67.4
	05:08-05:22	2.0	8.7	53.4
	05:22-05:37	2.3	9.5	51.1
	05:58-06:11	1.5	5.9	38.3
	06:11-06:25	1.5	6.9	46.0
	06:46-07:00	1.2	7.5	53.5
	07:00-07:14	1.7	7.1	55.3
	07:36-07:50	1.3	8.6	55.1

(continued)

Table A-1 (continued) - 9

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
18-AUG-86	07:51-08:06	1.3	8.9	58.3
	08:06-08:21	1.2	8.1	52.4
	08:21-08:36	1.2	9.5	43.8
	08:36-08:51	ND	10.2	49.1
	08:51-09:06	1.4	12.0	72.1
	09:06-09:21	1.9	15.5	106.4
	09:21-09:36	1.0	12.5	72.8
	10:05-10:20	ND	12.0	83.1
	10:20-10:35	ND	15.0	87.7
	10:35-10:50	ND	15.2	102.1
	10:50-11:05	0.9	16.4	101.0
	11:05-11:20	0.9	17.1	100.4
	11:20-11:35	ND	19.8	96.0
	11:35-11:50	ND	17.9	82.0
	11:50-12:05	ND	16.5	75.6
	12:05-12:20	ND	14.9	71.0
	12:20-12:35	ND	14.4	60.7
	12:35-12:50	ND	11.4	36.8
	12:50-13:05	ND	13.4	35.9
	13:05-13:20	ND	11.1	26.1
	13:20-13:35	ND	10.7	16.6
	13:35-13:50	ND	9.8	16.2
	13:50-14:06	ND	7.1	14.8
	14:06-14:21	ND	6.9	16.0
	14:21-14:36	ND	7.5	14.7
	14:36-14:51	ND	8.9	20.6
	14:51-15:06	ND	9.2	23.2
	15:06-15:21	ND	11.0	24.5
	15:21-15:38	ND	14.3	21.2
	15:38-15:53	ND	16.8	27.9
	15:53-16:08	ND	15.0	30.6
	16:08-16:23	ND	13.4	24.5
	16:23-16:38	ND	12.3	32.4
	16:38-16:53	ND	13.2	47.7
	16:53-17:08	ND	12.3	42.8
	17:08-17:23	ND	10.4	42.8
	17:23-17:38	ND	11.9	49.2
	17:38-17:53	ND	11.4	50.6
	17:53-18:08	ND	11.3	54.1
	18:08-18:23	ND	10.4	50.8
	18:23-18:38	ND	6.9	52.9
	18:38-18:53	ND	5.7	52.0
	18:53-19:09	ND	5.0	53.9
	19:31-19:42	ND	5.4	50.4
	20:05-20:11	ND	5.3	57.3

(continued)

Table A-1 (continued) - 10

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
18-AUG-86	20:32-20:43	ND	5.7	80.2
	21:04-21:15	1.0	6.9	63.3
	21:36-21:47	0.9	8.0	82.5
	22:10-22:24	1.8	7.8	74.1
	22:24-22:38	1.6	7.1	70.0
	22:59-23:13	1.5	7.2	68.3
	23:13-23:27	1.5	8.3	68.4
	23:48-24:00	1.5	8.4	64.4
19-AUG-86	00:00-00:02	1.5	8.4	64.4
	00:02-00:16	1.5	7.2	61.9
	00:37-00:51	1.7	7.7	56.4
	00:51-01:05	1.8	7.7	49.2
	01:25-01:39	2.0	8.4	46.6
	01:39-01:54	1.5	7.8	44.4
	02:14-02:28	1.2	8.6	27.1
	02:28-02:42	1.2	7.7	25.1
	03:03-03:17	1.2	7.8	26.7
	03:17-03:31	0.9	8.3	18.5
	03:52-04:06	ND	6.3	23.7
	04:06-04:20	ND	8.9	19.4
	04:41-04:55	ND	8.0	18.3
	04:55-05:09	ND	7.1	15.2
	05:30-05:44	ND	8.4	14.8
	05:44-05:58	1.0	9.6	27.6
	06:18-06:32	1.5	11.9	40.3
	06:32-06:47	1.5	9.2	41.6
	07:07-07:21	1.8	12.3	56.1
	07:21-07:35	1.6	11.4	65.6
	07:57-08:11	1.0	11.0	58.5
	08:11-08:26	ND	11.3	49.9
	08:26-08:41	ND	11.1	43.8
	08:41-08:56	ND	11.4	42.8
	08:56-09:11	ND	12.5	41.5
	09:11-09:27	ND	12.6	46.9
	09:27-09:42	ND	13.1	57.4
	09:42-09:57	ND	13.1	52.7
	09:57-10:13	ND	11.6	38.0
	10:13-10:28	ND	12.8	34.3
	10:28-10:43	ND	12.0	50.0
	10:43-10:58	ND	12.3	41.6
	10:58-11:13	ND	14.7	46.2
	11:13-11:28	ND	13.7	37.3
	11:28-11:43	ND	11.4	25.4
	11:43-11:58	ND	12.0	23.9

(continued)

Table A-1 (continued) - 11

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
19-AUG-86	11:58-12:13	ND	13.4	25.0
	12:13-12:28	ND	13.1	33.8
	12:29-12:44	ND	12.5	23.6
	12:44-12:59	ND	11.9	17.0
	12:59-13:14	ND	9.8	13.7
	13:14-13:29	ND	14.4	25.5
	13:29-13:44	ND	15.0	24.4
	13:44-13:59	ND	19.5	40.5
	13:59-14:14	ND	18.9	31.5
	14:14-14:29	ND	15.6	25.5
	14:29-14:44	ND	11.9	27.9
	14:44-14:59	ND	12.3	26.3
	14:59-15:14	ND	11.6	30.4
	15:14-15:29	ND	11.7	31.4
	15:29-15:44	ND	9.3	30.5
	15:44-15:59	ND	8.1	27.4
	15:59-16:14	ND	7.5	25.5
	16:14-16:29	ND	6.9	25.9
	16:29-16:44	ND	5.6	26.7
	16:44-16:59	ND	8.0	34.5
	17:04-17:19	ND	6.3	38.5
	17:19-17:34	ND	7.4	43.4
	17:34-17:49	ND	7.4	43.4
	17:49-18:04	ND	4.8	48.5
	18:04-18:20	ND	6.9	56.1
	18:20-18:35	ND	5.6	61.5
	18:35-18:50	ND	5.9	62.8
	18:50-19:05	ND	5.0	65.2
	19:05-19:20	ND	6.0	74.6
	19:42-19:53	ND	5.4	89.5
	20:14-20:25	0.9	5.4	82.6
	20:46-20:57	1.0	6.8	86.6
	21:18-21:29	0.9	5.9	80.8
	21:50-22:01	ND	5.3	76.1
	22:22-22:33	1.9	8.1	76.7
	22:54-23:05	2.1	9.9	68.8
	23:26-23:40	2.5	9.9	68.0
	23:40-23:54	2.0	9.2	60.5
20-AUG-86	00:15-00:29	1.8	9.5	58.5
	00:29-00:43	2.1	8.9	53.8
	01:04-01:18	2.1	9.8	47.2
	01:18-01:32	2.7	10.8	54.6
	01:53-02:07	1.7	9.5	36.7
	02:07-02:21	2.2	9.6	33.5

(continued)

Table A-1 (continued) - 12

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
20-AUG-86	02:41-02:55	1.3	9.3	19.3
	02:55-03:09	1.7	9.6	18.2
	03:30-03:44	1.8	10.4	20.5
	03:44-03:58	1.7	11.4	21.6
	04:14-04:33	2.1	10.1	20.9
	04:32-04:47	1.6	9.9	20.8
	05:03-05:21	1.8	10.5	25.9
	05:56-06:10	2.2	10.8	40.3
	06:10-06:24	2.1	9.2	44.0
	06:45-06:59	2.0	8.9	45.4
	06:59-07:13	3.1	12.8	52.7
	07:34-07:49	2.3	13.2	64.5
	07:49-08:04	1.9	13.1	71.9
	08:04-08:20	2.3	14.9	99.4
	08:20-08:35	2.5	16.7	116.2
	08:36-08:51	2.8	20.9	142.0
	08:51-09:06	2.0	18.3	138.1
	09:06-09:21	2.1	18.3	136.5
	09:21-09:36	1.8	17.1	12.9
	09:36-09:51	1.7	19.7	165.1
	09:51-10:06	1.4	18.8	173.7
	10:06-10:21	1.2	17.4	166.3
	10:21-10:36	1.3	16.2	141.5
	10:36-10:51	0.8	13.8	97.1
	10:51-11:06	ND	15.9	77.7
	11:06-11:21	ND	13.4	74.9
	11:36-11:51	ND	13.2	46.2
	11:51-12:06	ND	12.7	41.7
	12:06-12:21	ND	16.2	53.1
	12:21-12:36	ND	15.9	44.9
	12:36-12:51	ND	20.7	43.6
	12:51-13:06	ND	15.2	32.9
	13:06-13:21	ND	16.8	30.4
	13:21-13:36	ND	15.4	26.2
	13:36-13:51	ND	14.0	21.7
	13:51-14:06	ND	13.7	18.6
	14:06-14:21	ND	15.6	17.6
	14:21-14:36	ND	14.9	16.8
	14:36-14:51	ND	14.0	15.9
	14:51-15:06	ND	12.5	16.2
	15:06-15:21	ND	11.6	22.1
	15:21-15:36	ND	10.5	34.5
	15:36-15:51	ND	12.2	37.0
	15:51-16:06	ND	12.2	32.7
	16:06-16:21	ND	9.8	28.8

(continued)

Table A-1 (continued) - 13

Date	Scan Period PDT	Concentration (ppb) HONO	HCHO	NO_2
20-AUG-86	16:21-16:36	ND	9.5	30.9
	16:36-16:51	ND	8.7	29.3
	16:51-17:06	ND	6.8	25.8
	17:06-17:21	ND	6.8	32.5
	17:21-17:36	ND	7.5	40.4
	17:36-17:51	ND	8.7	40.9
	17:51-18:06	ND	8.7	43.6
	18:06-18:21	ND	9.2	57.0
	18:21-18:36	ND	8.4	59.8
	18:36-18:51	ND	9.6	67.5
	18:51-18:56	ND	11.0	75.4
	19:16-19:27	ND	7.7	83.6
	19:48-19:59	0.9	8.7	91.1
	20:20-20:31	1.0	7.4	89.0
	20:52-21:03	1.5	7.7	90.3
	21:23-21:35	1.2	7.4	85.7
	21:55-22:06	2.1	7.4	85.4
	22:28-22:42	1.1	7.4	73.6
	22:42-22:56	1.0	6.2	78.1
	23:16-23:30	1.8	10.2	84.6
	23:30-23:44	2.0	9.8	84.8
21-AUG-86	00:05-00:19	2.2	8.9	78.7
	00:19-00:33	2.4	11.0	78.8
	00:54-01:08	2.4	11.0	63.4
	01:08-01:22	2.4	10.5	56.2
	01:43-01:57	2.4	8.1	54.9
	01:57-02:11	2.6	8.7	57.4
	02:32-02:46	3.1	10.5	64.3
	02:46-03:00	2.7	9.9	56.6
	03:20-03:34	2.9	9.6	55.4
	03:34-03:48	3.4	10.8	75.6
	04:09-04:23	2.6	8.7	68.3
	04:23-04:37	3.3	7.5	62.2
	04:58-05:12	3.6	11.3	62.0
	05:12-05:26	3.6	11.1	59.8
	05:47-06:01	4.1	10.7	61.6
	06:01-06:15	4.2	10.5	61.1
	06:36-06:50	5.0	11.6	60.6
	06:50-07:04	4.0	12.8	61.6
	07:24-07:38	3.1	14.7	71.1
	07:38-07:53	2.6	13.4	81.8

[a]ND = below detection limit: 0.8 ppb for HONO,
4.5 ppb for HCHO
3.5 ppb for NO_2

APPENDIX B

PAH Concentrations Measured on the Low- and High-Flow Tenax Sampling Cartridges

Table B-1. Citrus College Glendora, CA, PAH Concentrations (Day 0800-2000 PDT, Night 2000-0800 PDT) Measured on Low-Flow Tenax

Date		Total Volume m^3	µg[a]									
			Naphthalene[b]	Back-up	2-Methyl-naphthalene	Back-up	1-Methyl naphthalene	Back-up	Biphenyl	Acenaph-thene	Fluorene	Phen-anthrene
8/12/86	Day	0.662	1.51	trace	0.18	-[c]	0.22	(0.11)	0.04	-[c]	0.04	trace
			1.41	"	0.15		0.20	(0.09)	0.03		0.06	0.01
8/12-13/86	Night	0.559	2.86	trace	0.50	trace	0.37	(0.14)	0.07	-	0.04	0.01
			2.70	0.04	0.46	(0.02)	0.33	(0.13)	0.06		0.06	0.02
8/13/86	Day	0.524	1.31	trace	0.07	-	0.17	(0.10)	0.01	-	0.03	trace
			1.21	0.01	0.04	-	0.16	(0.10)	0.02		0.05	"
8/13-14/86	Night	0.545	2.65	-	0.40	-	0.33	(0.11)	0.06	-	0.03	0.01
			2.53	-	0.39	-	0.32	(0.10)	0.05		0.06	0.02
8/14/86	Day	0.662	1.67	trace	0.11	-	0.18	(0.09)	0.02	-	0.03	trace
			1.61	-	0.09	-	0.18	(0.08)	0.02		0.06	0.01
8/14-15/86	Night	0.662	2.00	trace	0.45	-	0.34	(0.11)	0.04	-	0.03	0.01
			1.95	"	0.45		0.33	(0.10)	0.03		0.06	0.02
8/15/86	Day	0.607	1.71	trace	0.12	-	0.21	(0.11)	0.02	-	0.03	trace
			1.69	"	0.11	-	0.21	(0.10)	0.02		0.06	0.01
8/15-16/86	Night	0.517	2.16	-	0.37	-	0.29	(0.09)	trace	-	0.03	trace
			2.06	-	0.37		0.28	(0.09)	0.02		0.06	0.01
8/16/86	Day	0.469	1.53	trace	0.03	-	0.15	(0.11)	trace	-	0.03	trace
			1.44	"	0.03		0.14	(0.10)	0.01		0.05	"

(continued)

Table B-1 (continued) - 2

Date		Total Volume m^3	Naphthalene[b]	Back-up	2-Methyl-naphthalene	Back-up	1-Methyl naphthalene	Back-up	Biphenyl	Acenaph-thene	Fluorene	Phen-anthrene
							μg[a]					
8/16-17/86	Night	0.572	2.01 1.90	trace	0.39 0.36	-	0.31 0.29	(0.11) (0.09)	0.02 0.02	-	0.04 0.06	trace 0.01
8/17/86	Day	0.662	1.37 1.26	trace	0.04 0.03	-	0.16 0.14	(0.09) (0.08)	trace 0.01	-	0.03 0.06	trace
8/17-18/86	Night	0.628	2.76 2.60	trace	0.42 0.40	-	0.31 0.29	(0.10) (0.08)	trace 0.02	-	0.04 0.06	0.02 0.02
8/18/86	Day	0.517	2.20 1.99	trace	0.07 0.05	-	0.15 0.14	(0.10) (0.09)	trace 0.01	-	0.03 0.05	trace
8/18-19/86	Night	0.586	2.49 2.38	trace	0.32 0.31	(trace)	0.26 0.25	(0.10) (0.10)	0.01 0.02	-	0.04 0.06	0.01 0.02
8/19/86	Day	0.593	2.55 2.58	trace 0.02	0.07 0.06	(trace)	0.16 0.16	(0.11) (0.10)	trace 0.01	-	0.03 0.06	trace 0.01
8/19-20/86	Night	0.524	2.05 1.93	-	0.33 0.32	-	0.28 0.27	(0.11) (0.11)	trace 0.02		0.04 0.06	0.01 0.02
8/20/86	Day	0.490	2.04 1.95	trace 0.02	0.10 0.08	-	0.17 0.17	(0.08) (0.08)	trace 0.01	-	0.03 0.06	trace 0.01
8/20-21/86	Night	0.455	2.75 2.78	-	0.39 0.39	-	0.30 0.30	(0.07) (0.07)	0.01 0.02	-	0.04 0.06	0.01 0.02

[a]Values given are for replicate injections.
[b]Not corrected for small amount on back-up Tenax.
[c]None detected.

Table B-2. Citrus College, Glendora, CA, PAH Concentrations (Day 0800-2000 PDT, Night 2000-0800 PDT) Measured on High-Flow Tenax

Date		Total Volume m^3	μg[a] Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	Biphenyl	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene
8/12-13/86	Night	6.76	14.99	5.83	3.24	1.51	0.26	0.22	0.33	0.43
			14.57	6.35	3.46	1.51	0.27	0.21	0.33	0.43
8/13/86	Day	6.76	7.97	2.09	1.07	0.64	-[b]	0.02	0.20	0.17
			7.56	2.18	1.11	0.64	0.02	0.04	0.21	0.18
8/13-14/86	Night	6.83	12.83	4.75	2.53	1.16	0.08	0.15	0.25	0.34
			12.66	5.24	2.74	1.19	0.09	0.15	0.26	0.35
8/14/86	Day	6.83	5.70	1.73	0.90	0.48	-	0.02	0.20	0.14
			5.45	1.79	0.92	0.48	0.02	0.04	0.21	0.14
8/14-15/86	Night	6.83	11.22	4.23	2.19	0.71	0.15	0.11	0.23	0.27
			10.79	4.56	2.32	0.72	0.16	0.12	0.24	0.28
8/15-16/86	Night	6.83	13.76	4.75	2.50	0.45	0.06	0.14	0.23	0.28
			13.40	5.20	2.66	0.45	0.07	0.15	0.25	0.30
8/16/86	Day	6.69	4.66	1.32	0.64	0.34	-	-	0.15	0.10
			4.63	1.40	0.67	0.35	0.02	0.03	0.16	0.11
8/16-17/86	Night	6.83	12.60	4.57	2.29	0.66	-	0.16	0.27	0.25
			12.39	5.01	2.51	0.68	0.02	0.17	0.28	0.26
8/17/86	Day	6.34	2.99	1.02	0.47	0.23	-	-	0.17	0.12
			2.96	1.08	0.49	0.23	0.02	0.03	0.17	0.13

(continued)

Table B-2 (continued) - 2

Date		Total Volume m^3	μg[a] Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	Biphenyl	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene
8/17-18/86	Night	6.76	12.16 12.28	4.40 4.83	2.17 2.36	0.36 0.37	0.02 0.04	0.20 0.20	0.30 0.33	0.34 0.35
8/18/86	Day	6.42	4.30 4.31	1.61 1.74	0.78 0.81	0.27 0.28	- 0.02	0.02 0.04	0.19 0.21	0.16 0.17
8/18-19/86	Night	6.76	10.71 10.34	3.67 4.08	1.83 2.02	0.44 0.46	- 0.02	0.18 0.20	0.28 0.30	0.30 0.32
8/19/86	Day	6.76	3.43 3.38	1.27 1.37	0.60 0.62	0.24 0.25	- 0.02	0.02 0.04	0.15 0.16	0.14 0.15
8/19-20/86	Night	6.76	10.84 10.36	3.89 4.19	1.89 1.98	0.40 0.41	- 0.02	0.18 0.20	0.28 0.31	0.33 0.34
8/20/86	Day	6.76	5.52 5.41	2.11 2.27	1.00 1.06	0.36 0.36	- 0.02	0.03 0.05	0.22 0.23	0.19 0.20

[a]Values given are for replicate injections.
[b]Peak area too small for quantification.

Table B-3. Citrus College, Glendora, CA, PAH Concentrations Measured on Particles Collected on TIGF Filters

	μg[a]					Total Volume m^3
	Fluor-anthene	Pyrene	Benz(a)-anthracene	Chrysene/ Triphenylene	Benzo(a)-pyrene	
Filter Sample #1 8/13/86 0800-2000 hr[b]	0.90 0.95	1.86 1.88	0.58 0.68	1.86 2.22	0.80 0.92	4,078
Filter Sample #2 8/13-14/86 2000-0800 hr	0.93 1.04	1.27 1.35	0.79 0.85	2.83 3.12	1.89 2.06	4,078
Filter Sample #3 Day composite 8/15,16,17,18/86	2.76 2.91	2.76 2.80	1.25 1.35	3.67 4.14	1.64 1.38	13,050
Filter Sample #4 Night Composite 8/15-16,16-17,17-18,18-19/86	NQ[c] 2.11	NQ 3.34	0.73 0.83	3.34 3.62	1.88 2.13	13,050
Filter Sample #5 8/20/86 0800-2000 hr	1.24 1.10	1.22 1.38	0.40 0.47	1.72 1.77	0.71 0.80	4,078
Filter Sample #6 8/20-21/86 2000-0800 hr	0.87 0.95	0.99 1.00	0.58 0.55	1.62 1.68	0.77 0.84	4,078
Filter Sample #7 Repeat Dry Composite 8/15,16,17,18/86	1.50 1.62	1.55 1.76	0.64 0.66	2.76 2.88	0.83 0.95	5,158
Filter Sample #8 Repeat Night Composite 3/15-16,16-17,17-18,18-19	1.34 1.42	1.52 1.65	0.93 0.96	3.48 3.48	1.61 1.43	5,627

[a]Values given are for replicate GC/MS analyses.
[b]Times in PDT.
[c]NQ = Too low to quantify.

50272-101

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15. Supplementary Notes

16. Abstract (Limit: 200 words)

In the Carbonaceous Species Methods Comparison Study in August 1986 at Citrus College, Glendora, CA, the ambient concentrations of NO_2, HONO and HCHO were measured by long pathlength differential optical absorption spectroscopy (DOAS). Ambient concentrations of HNO_3, NH_3 and HCHO were measured by long pathlength Fourier infrared (FT-IR) absorption spectroscopy. Significant concentrations of these pollutants were observed, with mixing ratios of up to approximately 140, 4.5, 30, 20 and 15 parts-per-billion (ppb) for NO_2, HONO, HNO_3, HCHO and NH_3, respectively, being determined.

In addition, ambient air samples were collected during 12-hr daytime and 12-hr nighttime periods onto Tenax solid adsorbent, polyurethane foam (PUF) plugs and Teflon-impregnated glass fiber (TIGF) filters, and these samples were analyzed for mutagenicity and gas- and particle-associated polycyclic aromatic hydrocarbons (PAH) and nitroarenes. The mutagen densities obtained were consistent with those measured previously in the South Coast Air Basin. The following PAH and nitroarenes were observed and quantified: naphthalene, 1- and 2-methylnaphthalene, biphenyl, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benz(a)anthracene, chrysene/triphenylene, benzo(a)pyrene, 1- and 2-nitronaphthalene, 3-nitrobiphenyl, 2-, 3- and 8-nitrofluoranthene, and 1- and 2-nitropyrene.

17. Document Analysis a. Descriptors

Nitrous Acid
Formaldehyde
Nitrogen Dioxide
Ammonia
Polycyclic Aromatic Hydrocarbons
Nitroarenes
Mutagenicity

b. Identifiers/Open-Ended Terms

Long pathlength spectroscopy
Mutagenic activity of particulate ambient concentrations

c. COSATI Field/Group

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